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Recovery of Principal Organic Hazardous Constituents and Products of Incomplete Combustion from a Volatile Organic Sampling Train

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RECOVERY OF PRINCIPAL ORGANIC HAZARDOUS CONSTITUENTS AND PRODUCTS OF INCOMPLETE COMBUSTION FROM A VOLATILE ORGANIC SAMPLING TRAIN

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16. ABSTRACT The report describes an investigation of the recovery efficiencies of selected principal organic hazardous constituents (POHCs) from the Volatile Organic Sampling Train (VOST) under laboratory conditions. The compounds included: vinyl chloride, carbon tetrachloride, trichloroethylene, benzene, toluene, perchloroethylene, monochlorobenzene, methyl vinyl ketone, tetrahydrofuran, and chloroform. An in-house organic vapor generation system was used to produce atmospheres with predetermined concentrations of the POHCs. These were sampled by the VOST. The sampling traps were desorbed and analyzed by GC/FID. The predetermined total nanograms of POHCs were compared to the total nanograms found by the analyses. Excluding vinyl chloride and methyl vinyl ketone, the overall mean percent recovery for the individual compounds ranged from 81.0 to 118.1%. Vinyl chloride had an overall mean percent recovery of 55.2%, and methly vinyl ketone had an overall mean recovery of 37.8%. The mean percentage breakthrough of each compound past the first sampling trap, except vinyl chloride, ranged from 0.0 to 9.6%. Vinyl chloride had a constant breakthrough of 100%. The precision for the POHCs, including all compounds, was found to be 15.9%.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution	Pollution Control	13B
Organic Compounds	Stationary Sources	07C
Toxicity	Principal Organic Hazardous Constituents	06T
Sampling		14B
Volatility	Volatile Organic Sampling Train (VOST)	20M
Combustion		21B

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ABSTRACT

This task investigated the recovery efficiencies of selected POHCs from the Volatile Organic Sampling Train (VOST) under laboratory conditions. The compounds included vinyl chloride, carbon tetrachloride, trichloroethylene, benzene, toluene, perchloroethylene, monochlorobenzene, methyl vinyl ketone, tetrahydrofuran, and chloroform.

An in-house organic vapor generation system was used to produce atmospheres with predetermined concentrations of the POHCs. These were then sampled by the VOST. The sampling traps were desorbed and analyzed by GC/FID. The predetermined total nanograms of POHCs were compared to the total nanograms found by the analyses. Excluding vinyl chloride and methyl vinyl ketone, the overall mean percent recovery for the individual compounds ranged from 81.0% to 118.1%. Vinyl chloride had an overall mean percent recovery of 55.2%, while methyl vinyl ketone had an overall mean recovery of 37.8%. The mean percentage breakthroughs of each compound past the first sampling trap, except vinyl chloride, ranged from 0.0% to 9.6%. Vinyl chloride had a constant breakthrough of 100%. The precision for the POHCs, including all compounds was found to be 15.9%. Excluding methyl vinyl ketone and vinyl chloride, the overall mean accuracy for each compound ranged from -18.9% to +18.1%. Vinyl chloride had an overall mean accuracy of -44.8%, while methyl vinyl ketone had an overall mean accuracy of -62.2%.

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ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS:

BFB	---	bromofluorobenzene
CS_2	---	carbon disulfide
DI H_2O	---	deionized water
GC	---	gas chromatograph
GC/FID	---	gas chromatograph/flame ionization detector
GC/MS	---	gas chromatograph/mass spectrometer
I/I	---	inside/inside
MeOH	---	methanol
N_2	---	nitrogen
POHCs	---	principle organic hazardous constituents
QA	---	quality assurance
QC	---	quality control
RIC	---	reconstructed ion chromatogram
VOST	---	volatile organic sampling train

SYMBOLS:

@	---	at
°C	---	degrees celsius
g	---	gram
ng	---	nanogram
uL	---	microliter
ng/uL	---	nanogram per microliter
uL/min.	---	microliter per minute
mL/min.	---	milliliter per minute
Lpm	---	liter per minute
±	---	plus or minus
	---	sigma or standard deviation

1. INTRODUCTION

The objective of this task was to investigate the Volatile Organic Sampling Train (VOST) for recovery efficiencies of selected compounds. This was done under laboratory conditions at three (3) different concentration levels. These compounds included vinyl chloride, carbon tetrachloride, trichloroethylene, benzene, toluene, perchloroethylene (PERC), monochlorobenzene, methyl vinyl ketone, tetrahydrofuran, and chloroform. The expected amounts of each compound collected by the VOST traps ranged as follows: 400 ng to 800 ng for vinyl chloride; 9000 ng to 18000 ng for carbon tetrachloride; 2100 ng to 4200 ng for trichloroethylene; 1250 ng to 2500 ng for benzene; 500 ng to 1000 ng for toluene; 1850 to 3700 ng for perchloroethylene; 600 ng to 1200 ng for monochlorobenzene; 2500 ng to 5000 ng for methyl vinyl ketone; 1250 ng to 2500 ng for tetrahydrofuran; and 8500 ng to 17000 ng for chloroform.

To determine the selected compound recoveries, a Nutech VOST train with an in-house organic vapor generation system was used. The generation system, shown in Figure 1, was used to produce known steady-state levels of the chosen principle organic hazardous constituents (POHCs). The vaporized and gaseous POHCs were collected by the VOST train and concentrated in the polymeric resin, Tenax®. The traps were then separately thermally desorbed and analyzed using GC/FID and GC/MS detection. Control samples, treated identically as the VOST samples, were used as a check on the instrument calibration. Each sample and standard trap was spiked with a known amount of the internal standard, bromofluorobenzene (BFB). This provided additional analysis system checks. To determine the recovery efficiencies, the expected concentrations of the POHCs in the generation system were compared to that found by analysis. In addition, the percent breakthrough of any of the compounds past the first sample collection trap into the second or third trap was also determined.

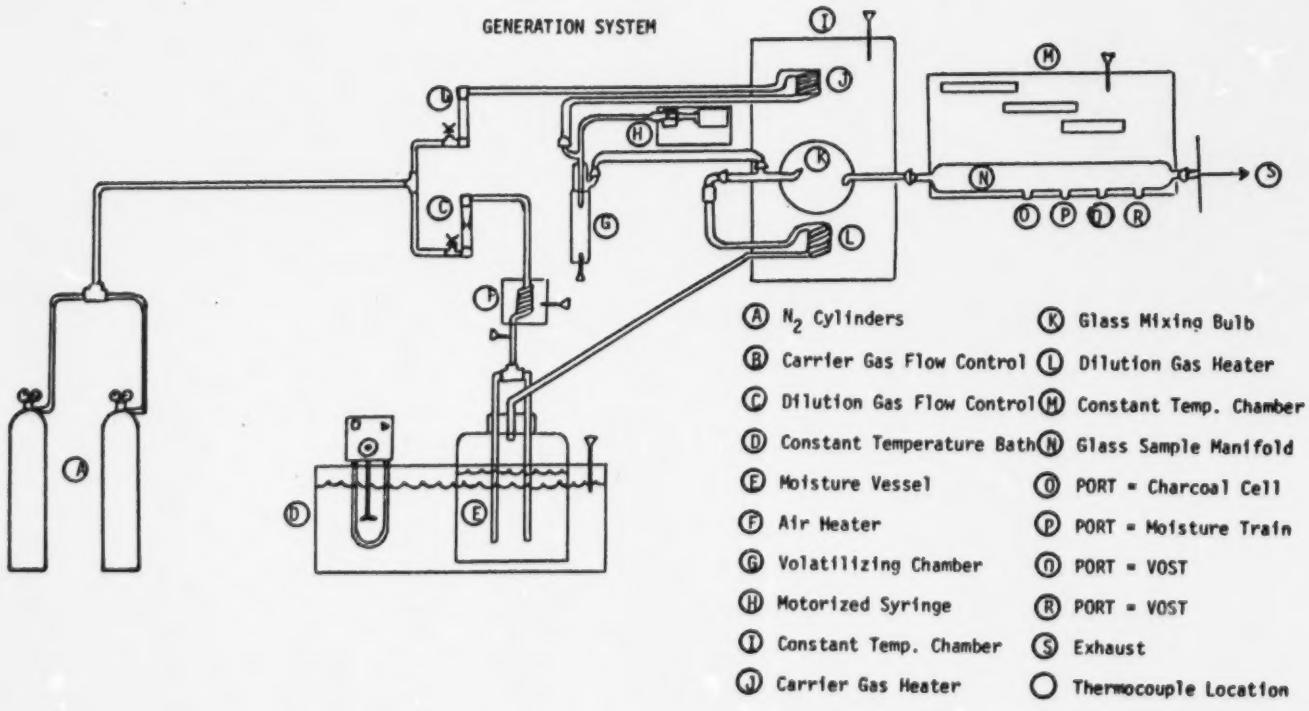


Figure 1. Organic vapor generation system.

2. CONCLUSIONS

The VOST evaluation determined that the recovery percentages of the compounds from the Tenax® and charcoal sample collection traps were high for all the POHCs studied, excluding methyl vinyl ketone and vinyl chloride. The overall mean percent recovery for the individual compounds ranged from 81.0% for tetrahydrofuran to 118.1% for chloroform, excluding those previously mentioned. Vinyl chloride had an overall mean percent recovery of 55.2%, while methyl vinyl ketone had an overall mean percent recovery of 37.8%. Additionally, the method was shown to have low percent breakthroughs past the first trap for all the standard POHCs, except vinyl chloride. The overall mean percent breakthroughs past the first trap ranged from 0.0% to 9.6%, excluding vinyl chloride, which had a constant breakthrough of 100%. The precision estimate for the POHCs, including all compounds, was found to be 15.8%. Excluding methyl vinyl ketone and vinyl chloride, the overall mean accuracy for each compound ranged from -18.9% for tetrahydrofuran to +18.1% for chloroform. Vinyl chloride had an overall mean accuracy of -44.8%, while methyl vinyl ketone had an overall mean accuracy of -62.2%.

As expected, low boiling POHCs, such as vinyl chloride, are difficult to quantitate by this technique.[1] As evidenced through sampling and analysis, the major reason for the poor recoveries of such compounds from charcoal is due to a varying desorption, as demonstrated by the varying responses of the internal standard. The calibration curves for such compounds, which adsorb mainly onto charcoal, should be developed on charcoal only, with no Tenax®. Thus, the characteristic desorption behavior from the sorbent would be known for both the compound and the internal standard. This would allow more accurate calibrations, and aid in the selection of an appropriate internal standard.

Although no desorption problems were found with methyl vinyl ketone based on the daily calibration checks, its stability in the POHCs standard was questionable. As discussed later, methyl vinyl ketone apparantly degraded in the solvent over a period of time, giving rise to eractic and poor recoveries over the entire range studied (nominally 2500 ng - 5000 ng).

Even though the method can be used to evaluate the POHCs content over a broad concentration range, the response curves of the POHCs must be well established. Compounds, such as carbon tetrachloride and chloroform, which demonstrated a non-linear response curve, should be restricted to the lower concentration range, where the response is generally more linear. A broad analysis range (nominally 8500 ng - 18,000 ng) should be used only with well defined response curves. As evidenced through calibration and analysis in this lab, sample results from non-linear calibration curves, which are poorly defined, could possibly be negatively or positively biased.

A leaking analytical system will also bias the sample results. Either sample loss or contamination by room air can negatively or positively bias the analytical results. The most likely place for leaks in the analytical system was found to be the desorption apparatus. The connections between the carrier gas, sampling traps, and the purging system are all susceptable to leaks due to the constant connection and removal of the VOST traps. The error thus introduced would have a significant effect on sample analysis results.

Another possible source of contamination and error, that can be improved, is the method used to load the internal standard or calibration standard onto a VOST trap, discussed later in greater detail. The trap is connected to a heated GC injection port which vaporizes the liquid standards and allows them to be purged onto the trap. The trap is then removed and reconnected to a cylinder in order to load any gaseous standards. The connections and removals of the sample traps, during spiking and desorption procedures, increase the possibility of sample loss or contamination by room air. Procedurally, the use of a gaseous multi-component standard would be advantageous by minimizing the possibility of sample loss or contamination, and for improved calibration development and quality control checks.

3. RECOMMENDATIONS

Based on the evaluation of the VOST method and on the resulting recoveries and breakthroughs of the studied POHCs, the following recommendations are made.

The first step of the analytical procedure should be a pressurization check of the desorption system. A leak free system is critical in order to eliminate any error due to sample loss, or sample contamination by the introduction of room air.

Second, the stability of the POHCs in the solvent media should be verified. Thus, any error due to compound degradation can be avoided.

Also, the utilization of a gaseous multi-component standard for calibration and quality control purposes should be considered in lieu of liquid standards where possible.

Finally, further investigation into the selection of sorbents for a greater efficiency in the collection and desorption of low boiling compounds such as vinyl chloride, should be considered.

4. ANALYTICAL PROCEDURES

The analytical procedures were designed to determine the recovery efficiencies from the VOST for vinyl chloride, carbon tetrachloride, trichloroethylene, benzene, toluene, perchloroethylene, monochlorobenzene, methyl vinyl ketone, tetrahydrofuran, and chloroform. The technique involved the analysis of Tenax® and charcoal VOST traps by thermal desorption followed by GC/FID analysis. A helium purge of the vaporized volatiles was bubbled through a water filled trap and collected on the analytical trap of the Purge and Trap system. This trap was then desorbed and analyzed by GC/FID.

The recovery efficiencies were determined at three (3) different concentration levels. Three (3) sampling runs were collected at each level. Each sampling run used three (3) sampling traps: two Tenax®-only traps and a charcoal-only trap.

For each concentration level, a single set of "blank" tubes was collected. This was accomplished by removing the end caps from the sorbent "blank" tubes for the same length of time necessary to insert and remove the "sample" tubes into and from the train.

4.1 Preparation of Sampling Traps

The Tenax®, and charcoal traps used were designed to accomodate standard 1/4" Teflon® filled ceramic ferrules (M-1 ferrules Supelco Inc.) and Swagelok® unions. These traps are shown in Figure 2. The traps were marked with an arrow to indicate the direction of sample flow. Thus, when the traps were returned to the laboratory for analysis, they could be oriented correctly for spiking and analysis.

Two (2) sampling traps were used for calibration and calibration checks: a Tenax® trap with 1.6 grams of Tenax®, and a Tenax®/charcoal trap with 1.0 gram of Tenax® and 1.0 gram of charcoal. These traps were used in tandem for all calibration spiking and desorption.

For the actual sampling runs, the Tenax®/charcoal trap was split into two (2) traps. The absorption of vinyl chloride onto the Tenax®-only traps could then be noted. The charcoal collected any vinyl chloride which was not retained by the Tenax®. The breakthrough of any of the other compounds

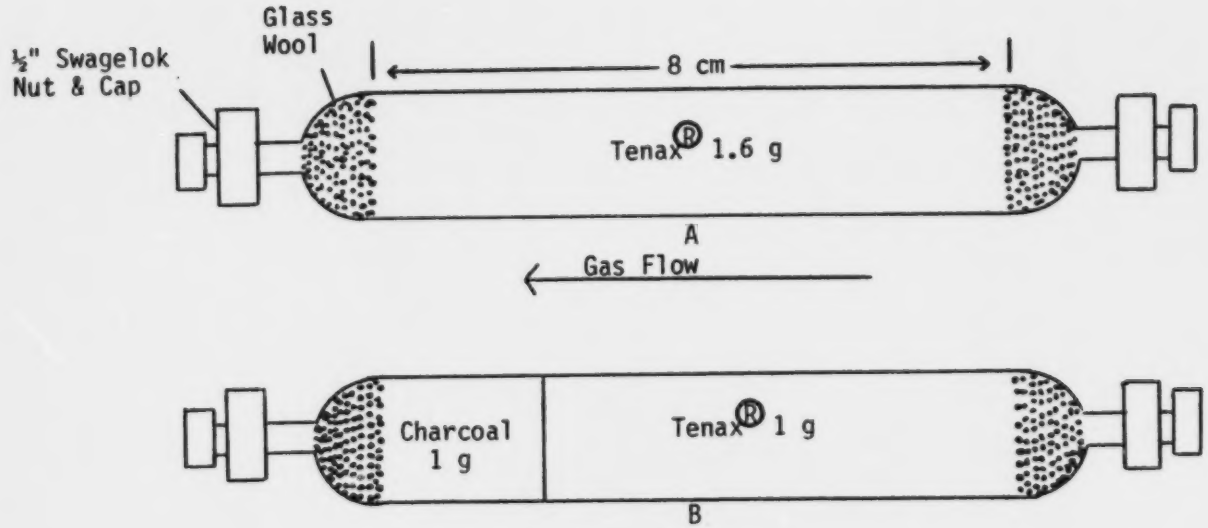


Figure 2. VOST inside/inside Tenax® traps.

past the first Tenax® trap to the second could also be noted. Thus, three (3) traps were used for each sampling: a Tenax®-only trap with 1.6 grams of Tenax®, a Tenax®-only trap with 1.0 gram of Tenax®, and a charcoal-only trap with 1.0 gram of charcoal.

The sorbent traps were prepared in the following manner. The Tenax® was cleaned by Soxhlet extraction first with methanol and then pentane for 24 hours each. The resin was dried in a vacuum oven with nitrogen purge for six (6) hours at 50°C. The tubes were then packed individually and thermally conditioned for twenty-four (24) hours at 200°C. This included the M-1 Ferrules and Swageloks®. While desorbing, hydrocarbon free nitrogen (or helium) flowed through the traps at 30 mL/min. Each tube was then subjected to a QC check using thermal desorption/cryogenic trapping followed by GC/FID analysis. The criteria for acceptable traps was 2 nanograms per compound with 10 nanograms total maximum allowable. Any tube that failed the QC check was re-desorbed for 24 hours and rechecked.

4.2 Sample and Standard Preparation

The POHCs standard was prepared by dilution of known amounts of each compound in methanol. All compounds except vinyl chloride were combined in one standard solution.

The stability of the methyl vinyl ketone in the standard was found to be of concern. The methyl vinyl ketone appeared to degrade to 3-methyl-buten-2-one. This possible degradation is further discussed in Section 5.2.

For vinyl chloride, a 1.041 ppm gas standard contained in a compressed gas cylinder was used. The standard was allowed to flow at a known rate either into the generation system with nitrogen dilution, or onto the calibration traps.

The same vinyl chloride and POHCs standards were used for both GC calibration and sample generation in the generation system. Thus, any error associated with the use of separate standard mixes was eliminated. All compound peak identifications were done by GC/MS and GC/FID as described in Section 5.1.

4.3 VOST and In-House Organic Vapor Generation System

To evaluate the VOST and chosen compound recoveries, a Nutech VOST train with the Inside/Inside design tubes and an in-house organic vapor generation system was used. Typical conditions used for each system are shown in Table 1.

Gaseous compounds like vinyl chloride were added to the generation system, shown in Figure 1, by using gas phase dilution. The liquid standard solution of POHCs was introduced into the generation system via a motor driven syringe. The syringe was weighed after filling it with the standard. It then slowly injected the standard over a period of time and was reweighed. The syringe flow rate was then calculated. Using the syringe flow rate, the vinyl chloride flow rate, and the total air flow, the theoretical concentration of each POHC in the sample manifold was found. Thus, predetermined steady-state levels of POHCs were produced. The total air flow was varied in order to change the concentration levels. To simulate certain stack conditions, moisture was added to the gas stream by passing the diluent gas (POHC free) through a heated water bath. The gaseous POHCs were then drawn into the VOST train, shown in Figure 3, and were collected onto the sampling traps.

Any portion of the generation system that contacted the POHCs was made of either Teflon® or glass. These portions were maintained above the boiling point of the highest boiling compound.

Samples were taken in triplicate. Three consecutive sets of tubes plus "blanks" were collected at each concentration level. A "set" was comprised of two Tenax® only tubes and a single charcoal only tube as described in Section 4.1. A nominal 20 liter sample was collected on each set of tubes over a time period of 20 minutes. The three sets are considered here to be replicates as the generation system was operated in a steady state mode. The traps were oriented so the sample went first through the 1.6 gram Tenax®-only trap, then the 1.0 gram Tenax®-only trap, and lastly the charcoal-only trap.

Table 1. VOST AND IN-HOUSE ORGANIC VAPOR GENERATION SYSTEM SAMPLING CONDITIONS

Sampling Train:	Nutech VOST with I/I design tubes
Generation System:	1 Lpm
Syringe flow rate:	2.18 uL/min.
Vinyl chloride flow rate:	111 mL/min. (of a 1.041 ppm tank)
Volatizing chamber flow rate:	0.95 Lpm
Average volume of air sampled:	20 L (nominal)
Oven temperature:	200°C
Volatizing chamber temperature:	170°C
Manifold temperature:	170°C
Temperature of line from manifold to sampling train:	284°C

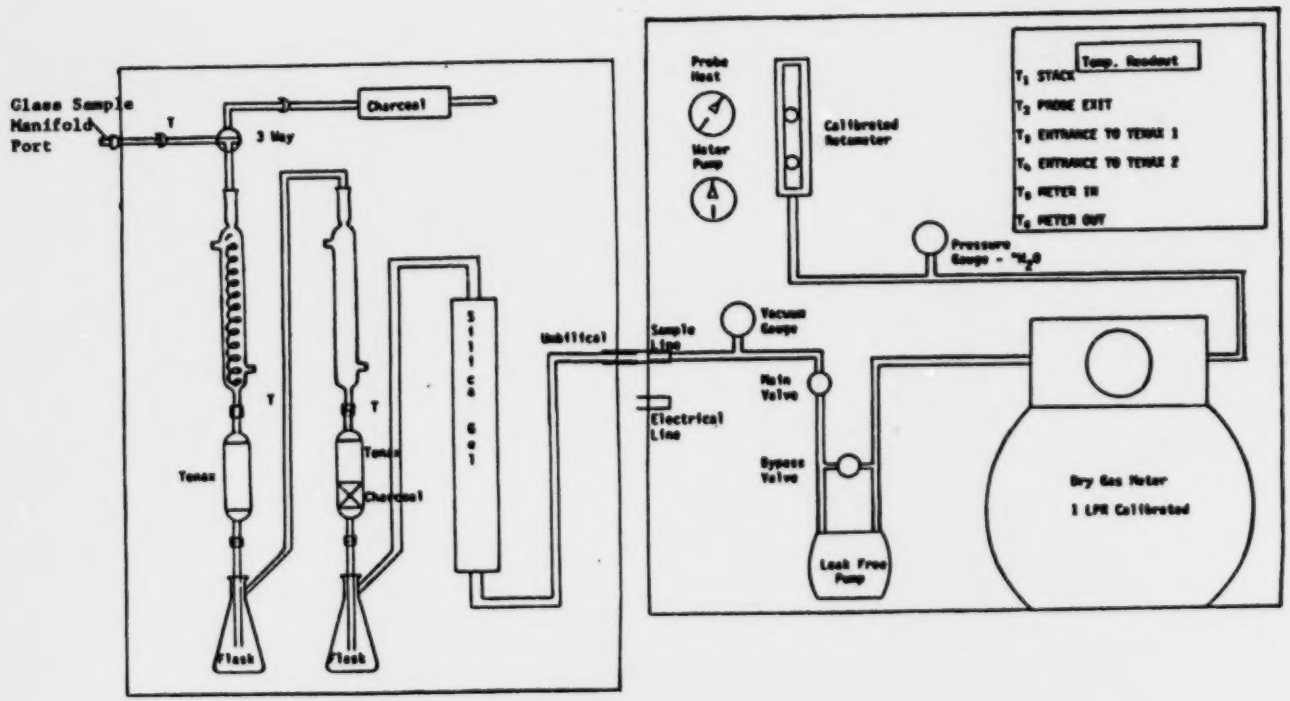


Figure 3. Schmatic of the VOST train and control module.

4.4 Internal Standard

Before analysis by GC/FID, or GC/MS, all traps, including blanks and calibration runs, were spiked with the internal standard, bromofluorobenzene (BFB). BFB was used so that the tuning of the mass spectrometer could be accomplished.

The BFB standard was prepared by dilution of a known amount of BFB into methanol. This standard was prepared and maintained separately from the POHCs standard. The concentration of the BFB was a nominal 400 ng/uL.

Each sampling trap was spiked using the following method. The trap was connected to a GC injection port kept at 150°C. The GC oven was left at room temperature. Using the solvent flush technique, 1 uL of BFB was injected, vaporized and collected onto the trap. Helium flow through the port was maintained at 50 mL/minute. The trap was removed after 2 minutes and analyzed by GC/MS, or GC/FID.

The BFB response for each analysis was monitored. For each set of results to be valid, the BFB response had to fall within a $\pm$ 3 limits from the overall BFB cumulative mean response.

4.5 Calibration

The analytical instruments were calibrated using the POHCs standard, the vinyl chloride standard, and the BFB internal standard. A four point calibration curve was initially established. Two-point calibration checks were performed both morning and evening of each day. For analysis to continue, the readings of these checks had to fall within the 95 percent confidence level relative to the calibration curve. Otherwise, the analyses stopped, and the system was checked until reproducible and acceptable results were obtained.

The POHCs standard and the BFB standard were vaporized directly onto the Tenax® and Tenax®/charcoal traps for calibration and calibration checks. The amount of POHCs standard injected was varied in order to achieve different loadings of each POHC. The same method used to load the internal standard was used here. After two minutes with helium flowing, the traps were then connected to the vinyl chloride gas cylinder.

The vinyl chloride, flowing at a known rate, flowed directly onto the traps for a measured amount of time. The time of flow was varied in order to load different amounts of vinyl chloride. These traps were then removed and analyzed.

A linear response curve over a wide range (nominally 1000 ng - 11000 ng) was not found for all the selected compounds, as discussed in Section 5.3.

4.6 Analysis of VOST Traps

The VOST sampling traps were analyzed by thermal desorption based on EPA Method 624. The single Tenax® traps, single charcoal traps, and (tandem Tenax® and charcoal traps) were all analyzed in the same manner. Prior to analysis, the Tekmar® purge and trap apparatus was modified, allowing the sorbent traps to be connected to the purge and trap apparatus, as shown in Figure 4. The step-by-step procedure used for the analyses is:

(1) The GC/MS, or GC/FID was set to its analytical conditions. The conditions used are shown in Tables 2 and 3, respectively.

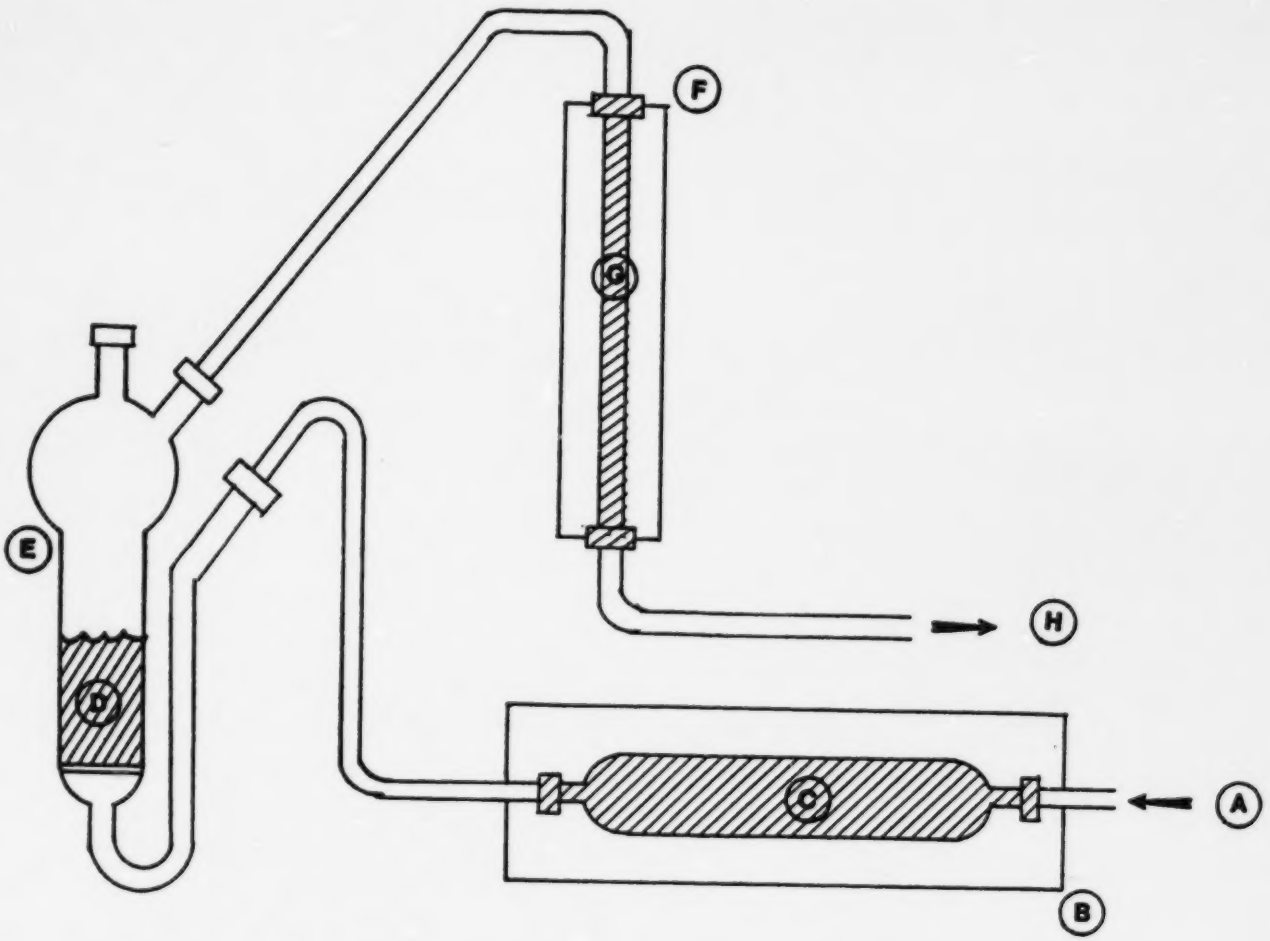
(2) A maximum of 1.0 uL of methanol was drawn into the syringe followed by 1.0 uL of the internal standard. For calibration runs and checks, 1.0 uL of the POHC standard followed the internal standard.

(3) The sampling trap end plugs were removed. The trap was then attached to a GC injection port heated to 150°C. The trap was oriented so that the carrier gas flowed in the same direction as the sample gas during sampling.

(4) The syringe contents were injected. The carrier gas, helium, was then allowed to flow at 50 mL/minute for 120 seconds.

(5) For vinyl chloride calibration runs and checks, the trap was disconnected and connected to the vinyl chloride gas cylinder. The vinyl chloride flowed onto the trap for a measured amount of time at a known rate.

(6) The trap was connected to the modified purge and trap apparatus, and oriented so the carrier gas flowed in the direction opposite to that used during sampling.



A = N_2 carrier gas flow
B = Thermal desorption chamber
C = VOST trap
D = Organic free DI H_2O
E = Sparger
F = Heating trap cover
G = Supelco trap # 2-0294
H = To GC

Figure 4. Modified purge and trap apparatus.

Table 2. GC/MS ANALYTICAL CONDITIONS

Instrument:	Finnigan 4000 Gas Chromatograph/ Mass Spectrometer
Data System:	INCOS
Column:	1% SP.1000 60/80 Carbopack® B, in a 2mm ID x 8' glass tube
Temperature Program:	30°C (3 minutes) to 190°C (15 minutes) at 10°C/minute
Injection Type:	Tekmar® switching valve
Source Temperature:	260°C
Injector Temperature:	190°C
Scan Range:	Low Mass: 40 High Mass: 450 Rate: 2 s/scan
Carrier Gas:	Helium at 30 mL/minute

Table 3. GC/FID ANALYTICAL CONDITIONS

Instrument:	Varian 3700 Gas Chromatograph
Detector:	FID with 0.2 inch quartz flame tip
Column:	1% SP-1000 on Carbopack® B 60/80 8 feet x 1/8 inch SS
Temperature Program:	40°C (7 minutes) to 220°C (13 minutes) at 15°C /minute
Attenuation:	10^{-11} Amps
Carrier Gas:	Nitrogen at 25 mL/minute
Flame Gases:	Air at 300 mL/minute Hydrogen at 30 mL/minute
Peak Threshold Limit:	500 area counts

(7) All fittings were checked to be leak free. 5 mL of organic blanked water was put into the sparger.

(8) The trap was then placed in the prebeated thermal desorption chamber and heated to 190°C.

(9) The purge timer was started for a 15 minute purge. The purge and trap conditions are shown in Table 4.

(10) As the sample desorbed, the instrumentation was set to the initial conditions.

(11) As the purge cycle ended and the purge and trap apparatus began the desorb cycle, the GC temperature program was initiated. If the GC/MS was being used, the MS data aquisition was also started. The purge and trap analytical trap desorbed for 4 minutes.

(12) Steps two (2) through eleven (11) were repeated for the remaining sample traps.

Each set of traps was analyzed in the following order: charcoal-only trap, 1.0 gram of Tenax®-only trap, and 1.5 grams of Tenax®-only trap. This order is opposite to the sampling orientation. Thus, the traps with lower POHC's content were run first to minimize sample carry-over from higher content sample runs.

Table 4. PURGE AND TRAP CONDITIONS

Instrument:	Tekmar® Purge and Trap Model LSC-2
Trap:	Supelco® Trap # 2-0294 1 cm 3% SP-2100 60/80 Chromosorb® WAW Inlet; 7.7 cm 60/80 Tenax® GC; 7.7 cm PW 35/60 Silica Gel Gd-15; 7.7 cm PW 20/50 Charcoal Method 601 outlet.
Purge Temperature Program:	Purge ready @ 30°C (purge 11 minutes) GC oven initially @ 44°C Purge Trap Desorb Preheat to 100°C Desorb final @ 180°C (4 minutes) Bake trap @ 180°C (8 minutes)
Carrier Gas:	Nitrogen @ 30 mL/minute
Thermal Desorption Chamber:	Supelco® Carrier Gas Purifier Oven
Desorption Chamber Temperature:	190°C

5. RESULTS AND DISCUSSION

To evaluate the VOST for recovery efficiencies of the selected POHCs, predetermined amounts of POHCs were sampled by the VOST and the VOST traps then analyzed. The expected nanograms of each POHC were compared to the total nanograms found by GC/FID.

5.1 Peak Identification

The POHCs standard, vinyl chloride standard, and internal standard were analyzed by GC/MS and GC/FID for peak identification. Using common syringe techniques, 1 uL of the POHCs standard and 1 uL of the internal standard were injected into 5 mL of organically blanked deionized H_2O. The DI H_2O was then loaded into the sparger of a Tekmar® Purge and Trap apparatus. Using a helium purge, the volatile POHCs were removed from the DI H_2O, loaded onto the GC column, and analyzed by GC/MS. The peaks of the POHCs standard were identified as shown in Figure 5. The POHCs standard and the internal standard were then directly injected onto the GC column and analyzed by GC/FID. Using the retention times and chromatogram from the GC/MS identification, the GC/FID peaks were identified as shown in Figure 6. To identify the vinyl chloride peak, the POHCs standard, the vinyl chloride standard and the internal standard were injected onto a VOST trap attached to a GC injection port. The trap was then desorbed and analyzed by GC/FID. The additional vinyl chloride peak was identified as shown in Figure 7.

5.2 POHCs Standard Stability

The stability of the methyl vinyl ketone in the POHCs standard was found to be of concern. The methyl vinyl ketone appeared to degrade to 3-methyl-3-buten-2-one, as determined by GC/MS.

The peak area counts of several methyl vinyl ketone injections were compared over a period of time. The total area counts of methyl vinyl ketone consistently decreased, while an unidentified peak consistently increased. This peak, shown in Figure 8, eluted just after benzene. After a period of time, the degradation of methyl vinyl ketone apparently ceased, possibly reaching an equilibrium.

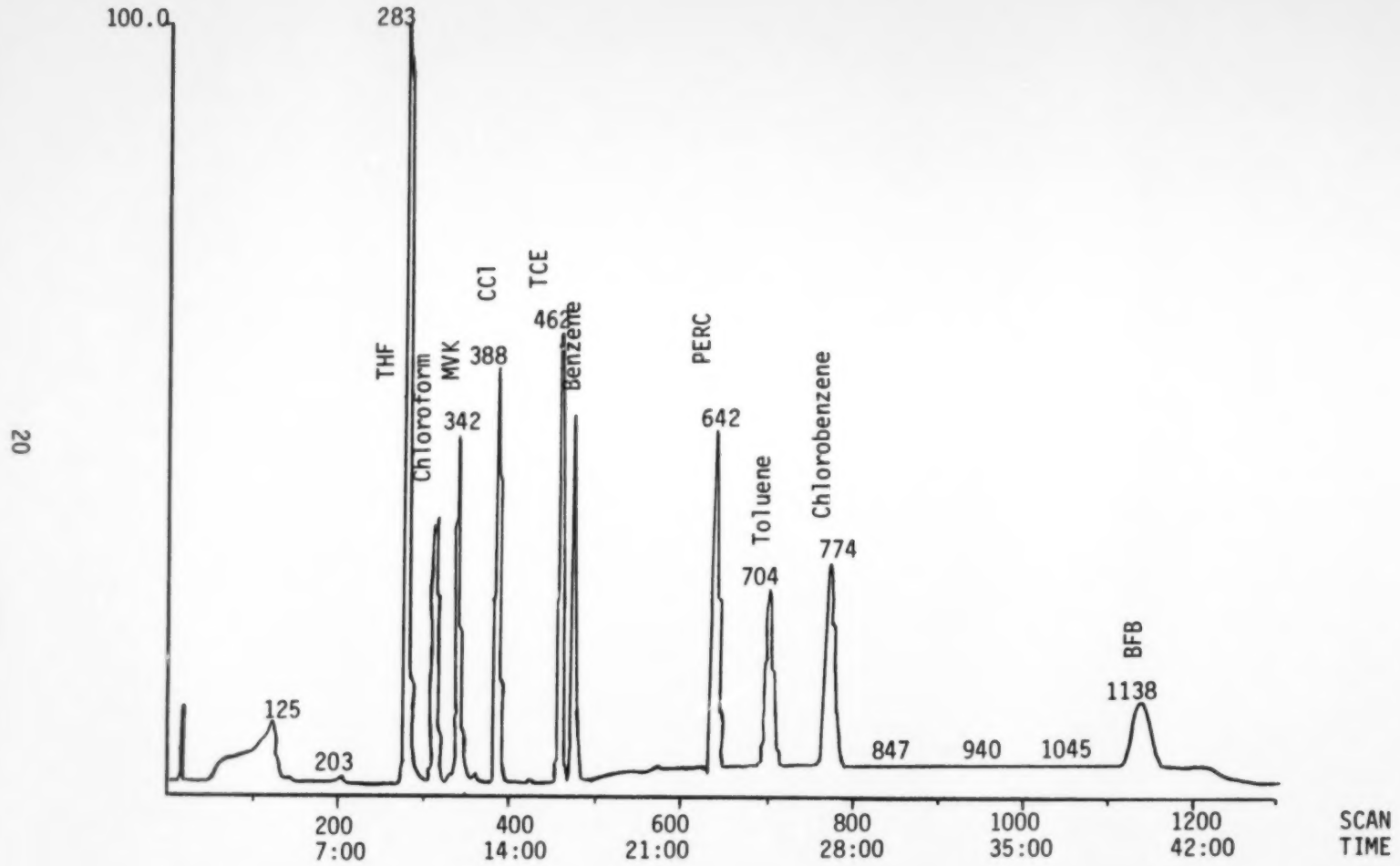


Figure 5. Peak identification of the POHCs standard by GC/MS.

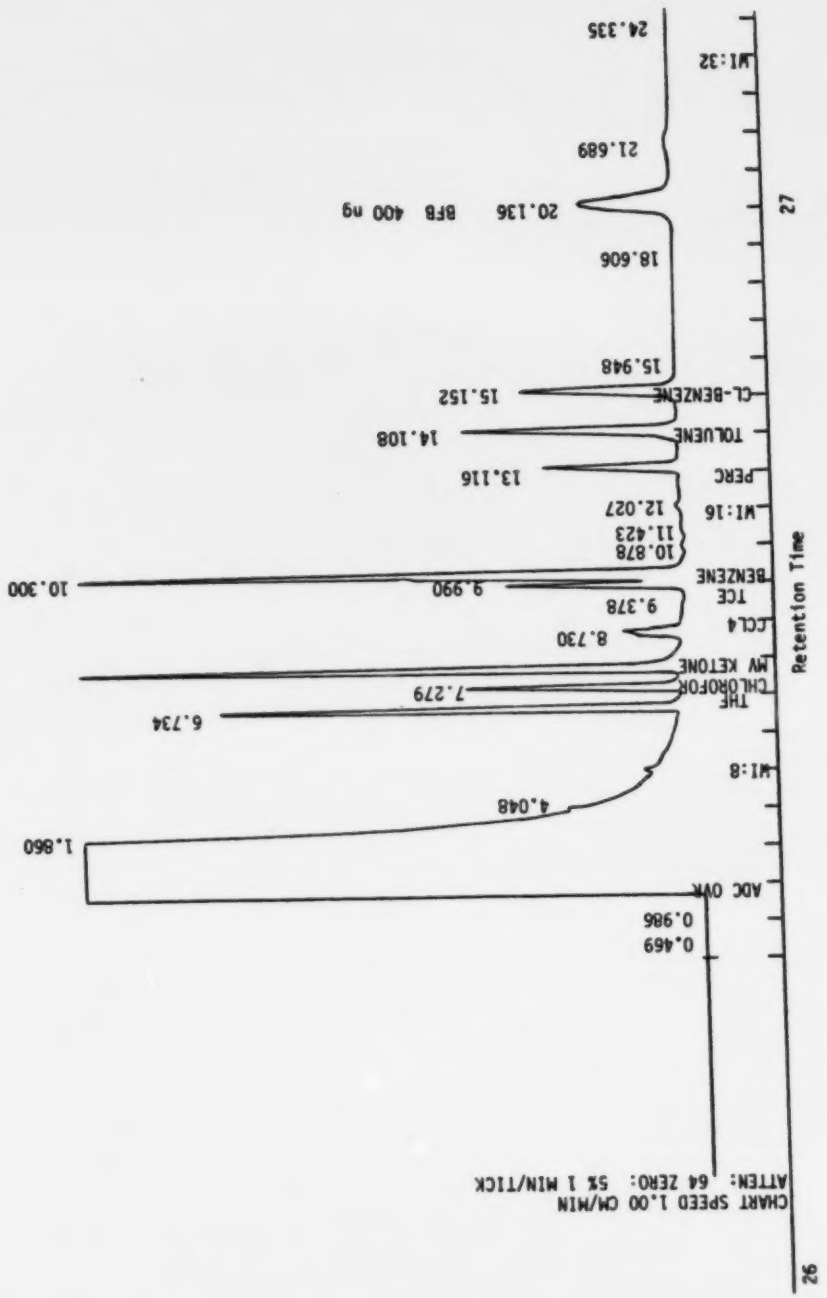


Figure 6. Peak identification of the POHCs standard by GC/FID.

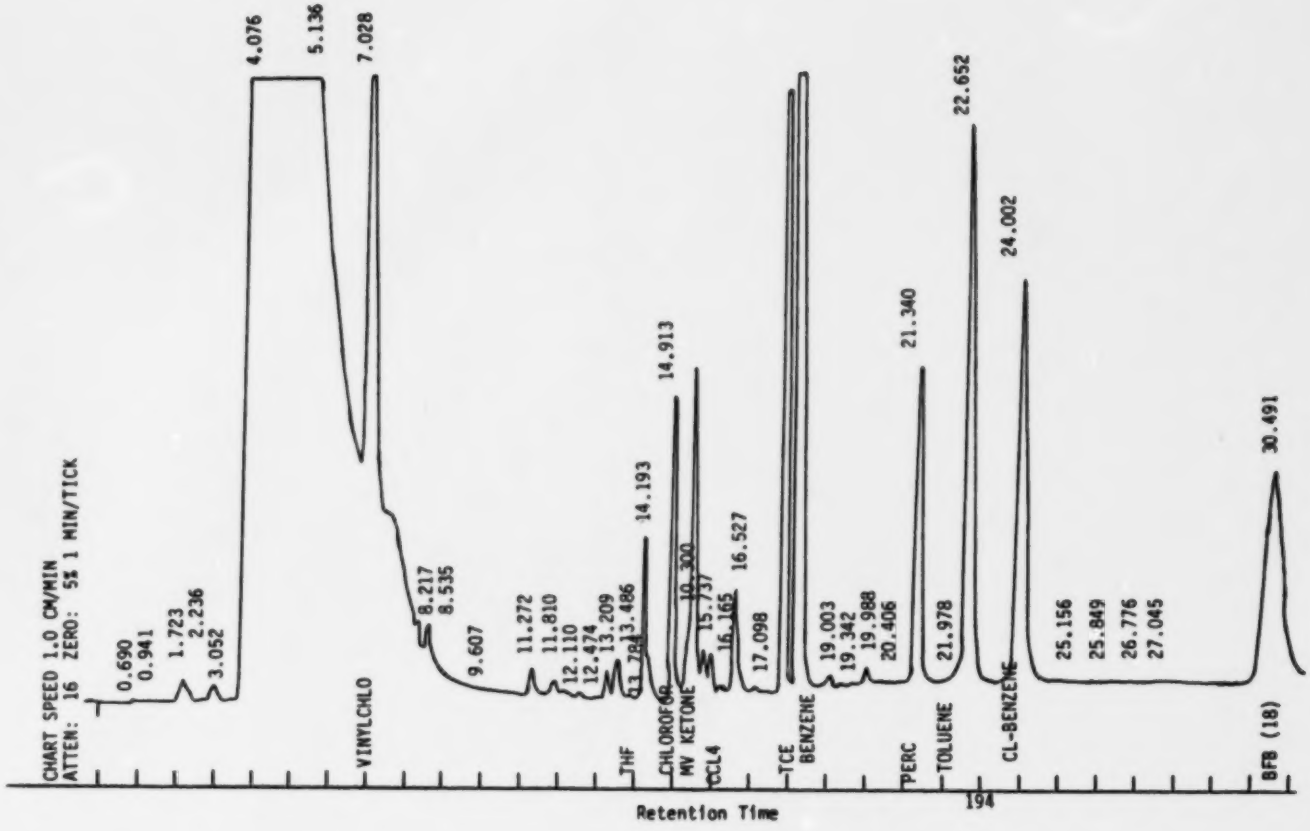


Figure 7. Peak identification of the POHCs and vinyl chloride standard by GC/FID.

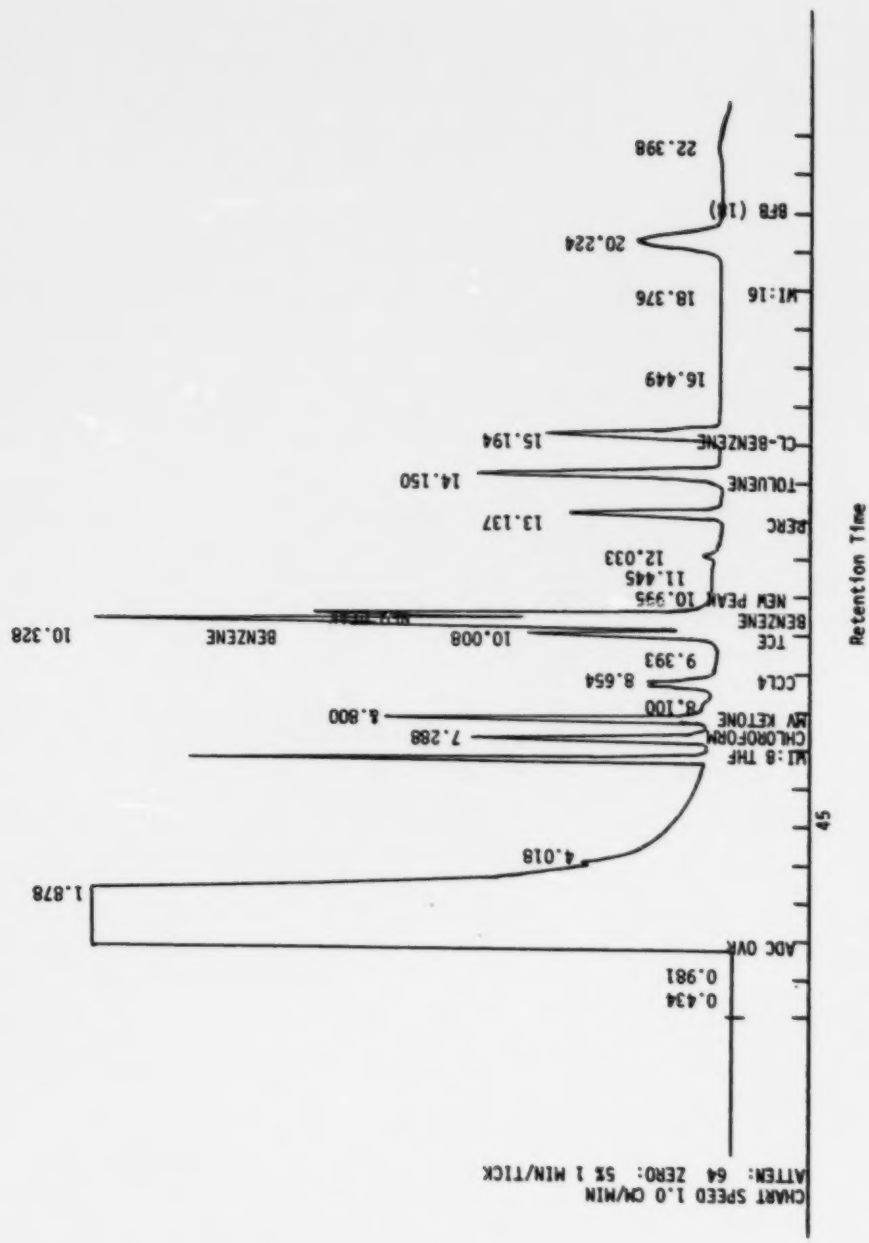


Figure 8. GC/FID analysis of POHCs standard showing newly evolved peak.

The POHCs standard was then analyzed by GC/MS for the identification of the newly evolved peak. The POHCs standard reconstructed ion chromatogram (RIC), shown in Figure 9, did not show a prominant peak from GC/MS. An enlarged RIC showed a small peak eluting at scan 484, shown in Figure 10. The GC/MS identification, shown in Figure 11, did not have a good match between the peak's chromatogram and any of the three closest matching compound chromatograms. The third ranked match, 3-methyl-3-buten-2-one, implied that methyl vinyl ketone could be combining with the solvent, MeOH, and gaining a methyl group. No further work towards peak identification was done. Still, the degradation of methyl vinyl ketone is a problem, and should be further investigated should additional work be done using this particular POHC.

5.3 Calibration Curves

After the identification of the POHCs by GC/FID, the response curve for each compound was determined. Varying amounts of each compound were analyzed by GC/FID. The response curves were determined by comparing the varied amounts of each compound injected with the resulting area counts.

Four different amounts of the POHCs standard were injected and compared: 0.3 ul, 1.0 ul, 2.0 ul, and 6.0 ul. The highest calibration point was selected to bracket the expected maximum sample range. A minimum of three injections were made for each calibration volume. The resulting GC area counts were then averaged. The nanograms of each compound (per injected amount), and the resulting GC/FID area counts are shown in Table 5. Due to the non-linear responses from carbon tetrachloride and chloroform, curves were nominally fitted to the data from these compounds. The remaining calibration curves were fitted using linear regression. Calibration curves are shown in Figures 12 through 21. The correlation coefficients, slopes, and intercepts of these curves are listed in Table 6.

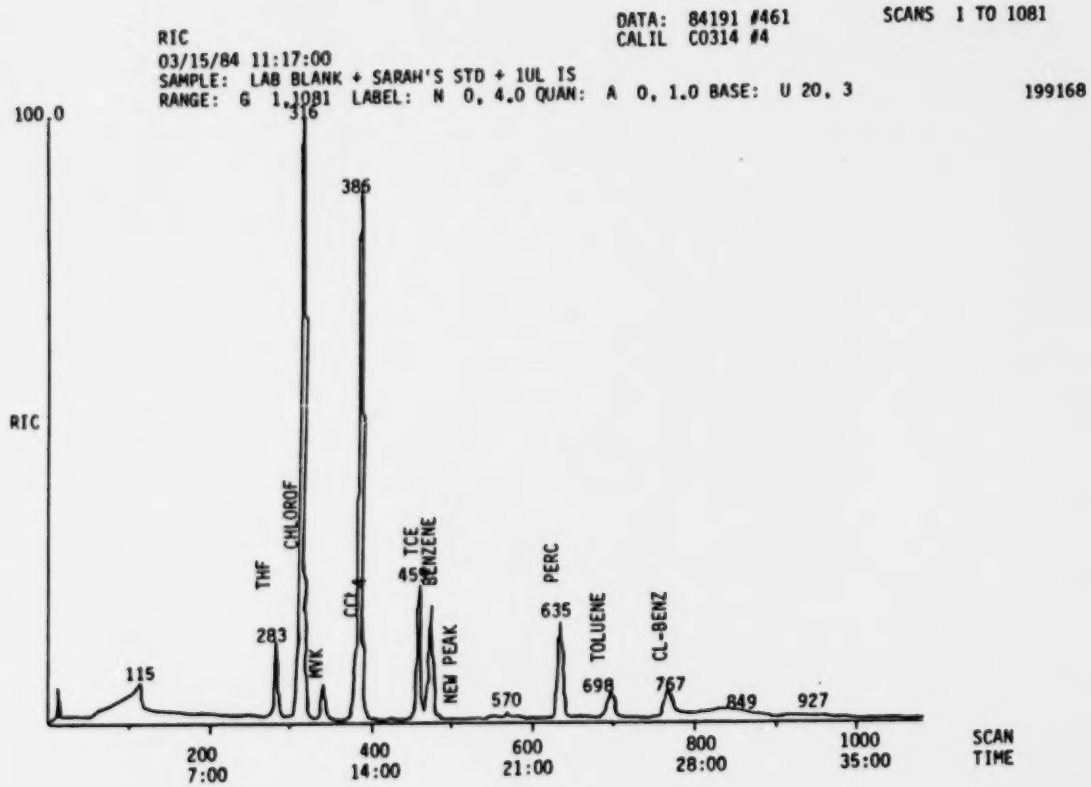


Figure 9. GC/MS analysis of POHCs standard for identification of newly evolved peak.

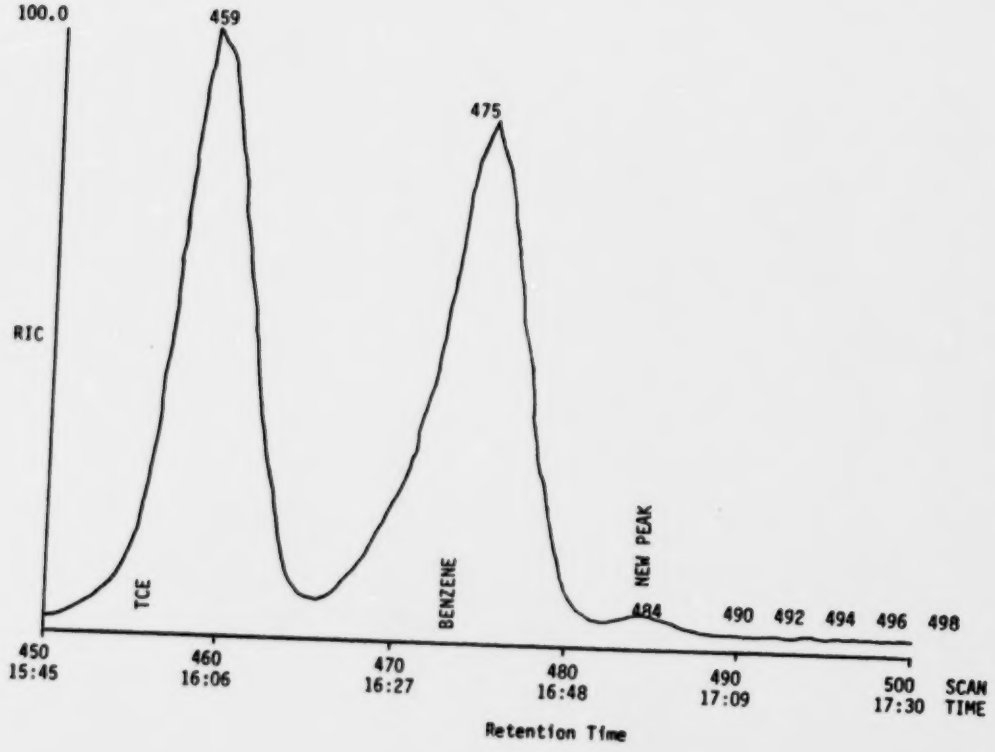


Figure 11. GC/MS identification of newly evolved peak from POHCs standard.

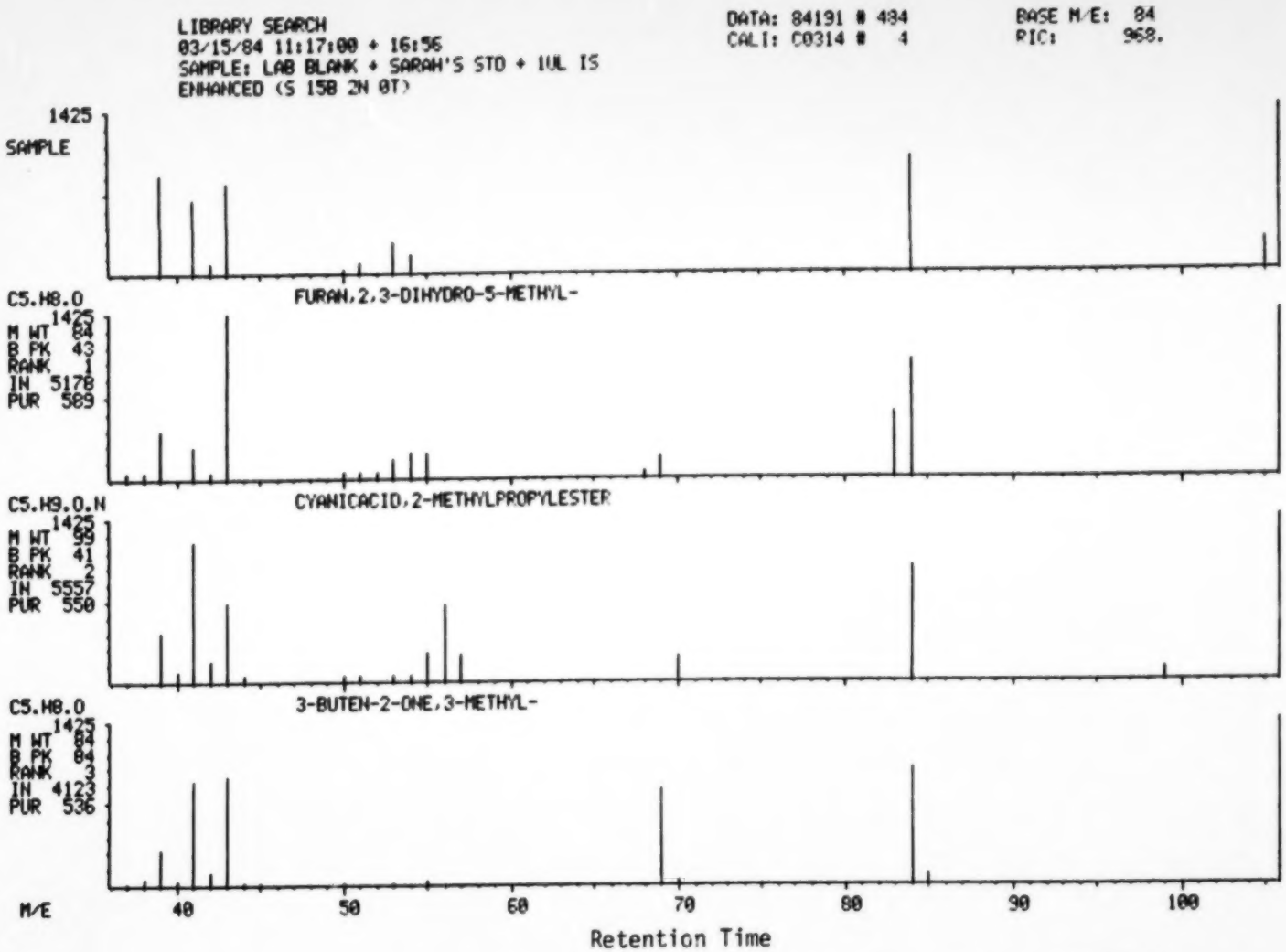


Figure 11. GC/MS identification of newly evolved peak from POHCs standard.

Table 5. POHCs' CALIBRATION DATA

Resulting Compound Amount and Corresponding GC area Counts		Injection Volumes (ul)			
		0.3	1.0	2.0	6.0
Benzene	Amount (ng)	131.1	437.0	874.0	2622
	Area Count (AC)	202286	501429	888166	2704748
Carbon tetrachloride	Amount (ng)	956.4	3188	6376	19128
	Area Count (AC)	12866	24419	32653	284842
Chloroform	Amount (ng)	865.2	2884	5768	17304
	Area Count (AC)	17858	54017	92386	630369
Methyl Vinyl Ketone	Amount (ng)	259.0	864.0	1728	5184
	Area Count (AC)	24915	57962	84424	143005
Monochlorobenzene	Amount (ng)	66.30	221.0	442.0	1326
	Area Count (AC)	54822	156433	289750	865438
Perchloroethylene	Amount (ng)	194.7	649.0	1298	3894
	Area Count (AC)	30140	79788	155490	486404
Tetrahydrofuran	Amount (ng)	132.0	440.0	880.0	2640.
	Area Count (AC)	18352	37164	66771	191899
Toluene	Amount (ng)	51.90	173.0	346.0	1038
	Area Count (AC)	69899	178301	331730.	973319
Trichloroethylene	Amount (ng)	219.3	731.0	1462	4386
	Area Count (AC)	35733	97145	188174	574898
Vinyl Chloride	Amount (ng)	209.0	500.0	980.6	1506
	Area Count (AC)	67465	210776	459004	508066

Table 6. LINEAR REGRESSION DATA FOR POHCs' CALIBRATION CURVES

Compound	Correlation Coefficient	Slope	Y-Intercept	X-Intercept
Benzene	0.99956	1017	32582	-32.03
Carbon tetrachloride	--*	--*	--*	--*
Chloroform	--*	--*	--*	--*
Methyl Vinyl Ketone	0.9522	25.05	21789	-869
Monochlorobenzene	0.99987	647.2	7217	-11.15
Perchloroethylene	0.99976	124.0	542.8	-4.37
Tetrahydrofuran	0.99909	70.99	4734	-66.68
Toluene	0.99977	926.5	12511	-13.50
Trichloroethylene	0.99988	130.3	1951	-14.96
Vinyl Chloride	0.9717	363.9	16520	-45.40

*Non-linear response.

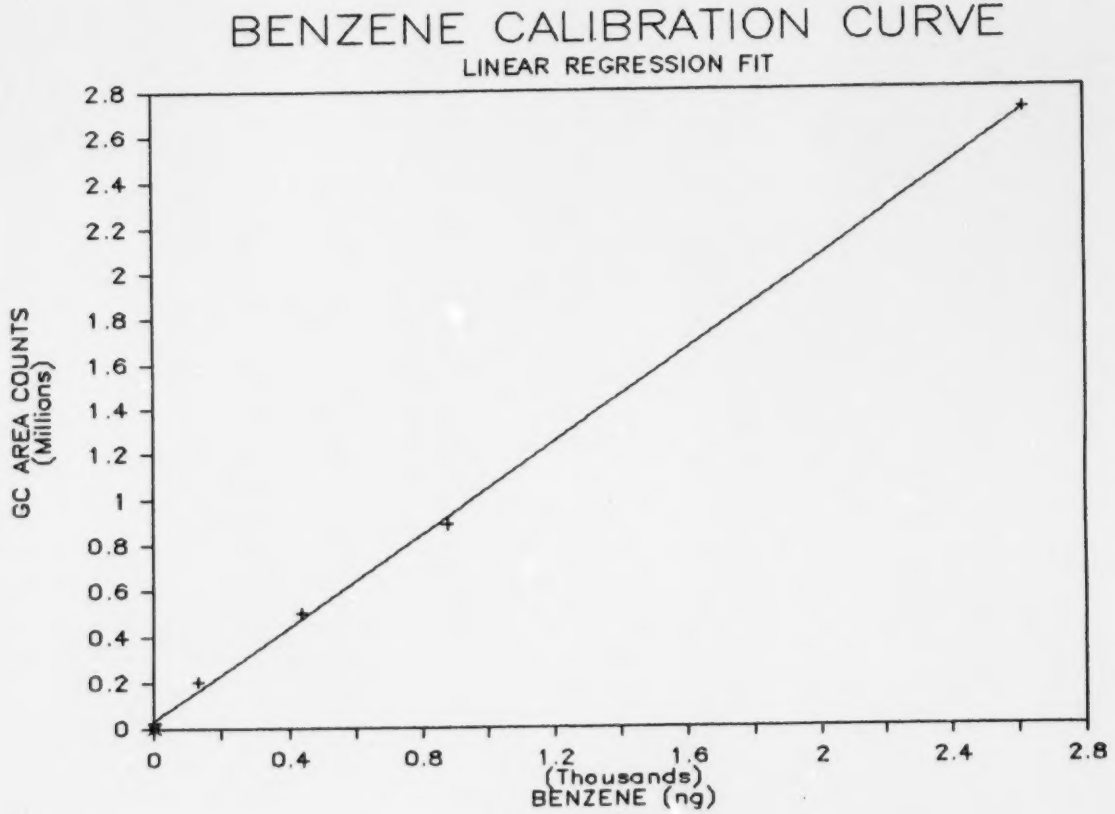


Figure 12. Calibration curve for benzene.

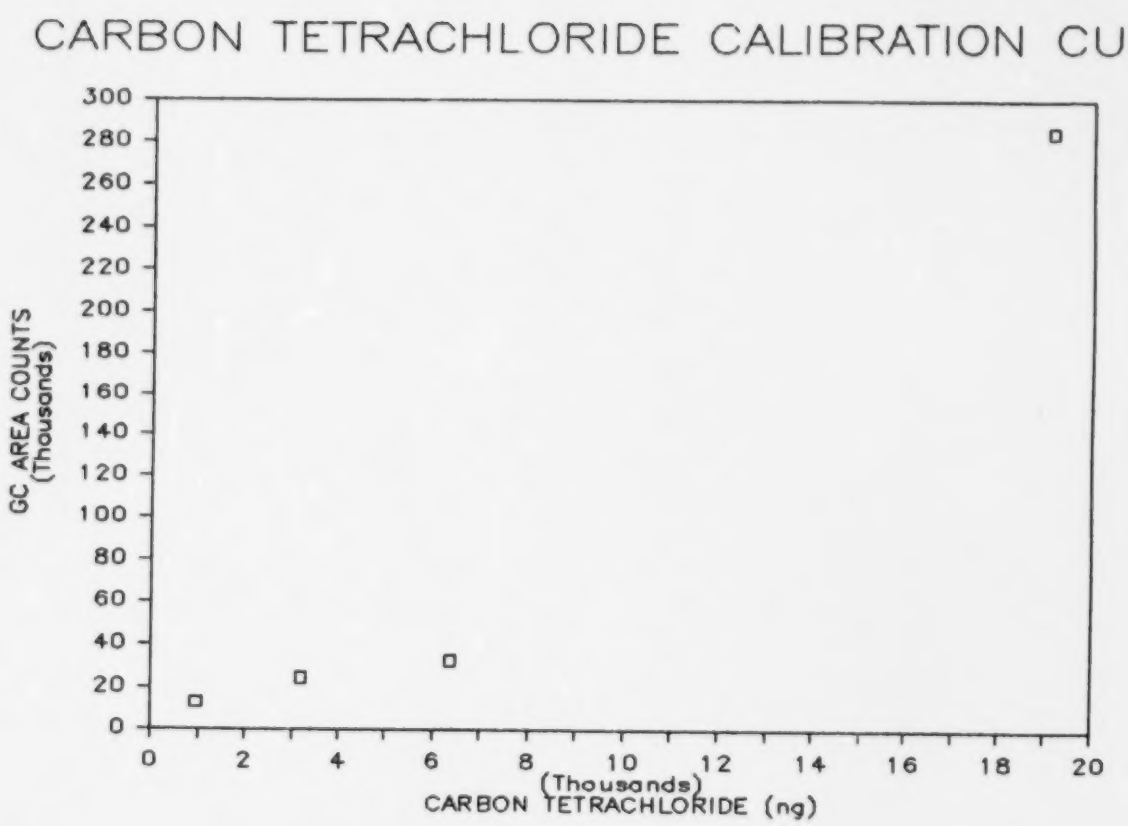


Figure 13. Calibration curve for carbon tetrachloride.

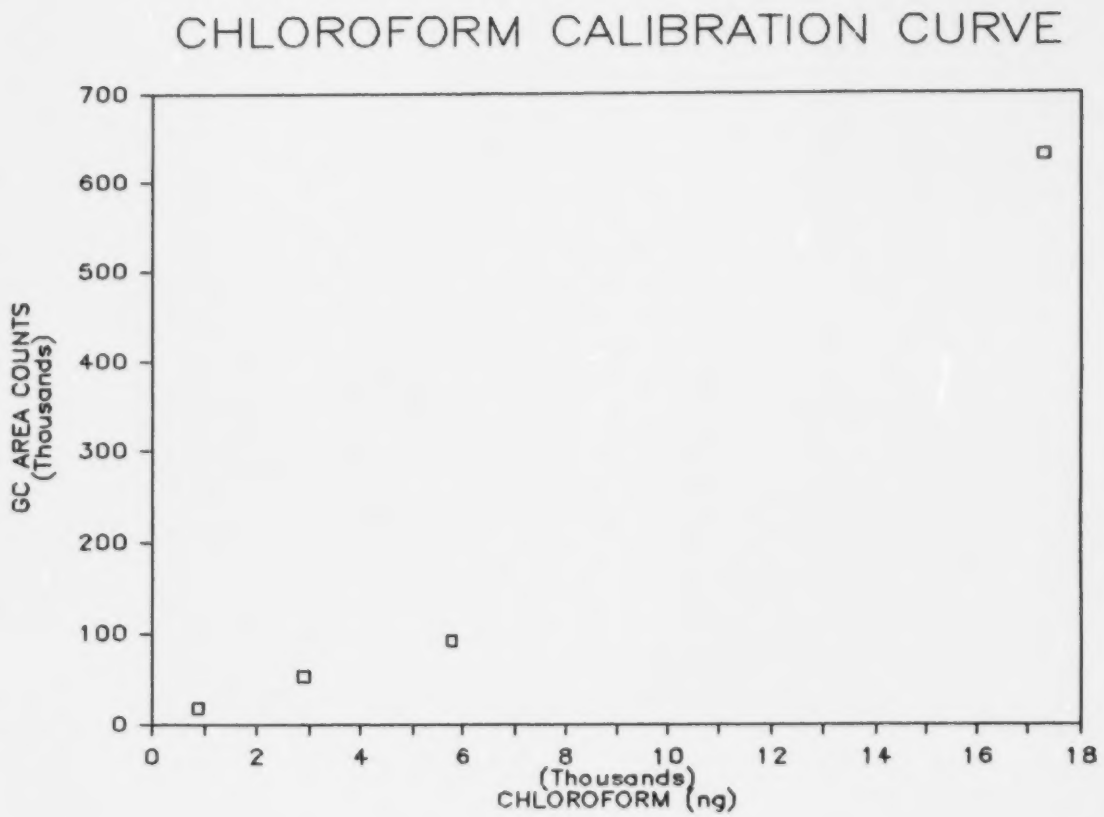


Figure 14. Calibration curve for chloroform.

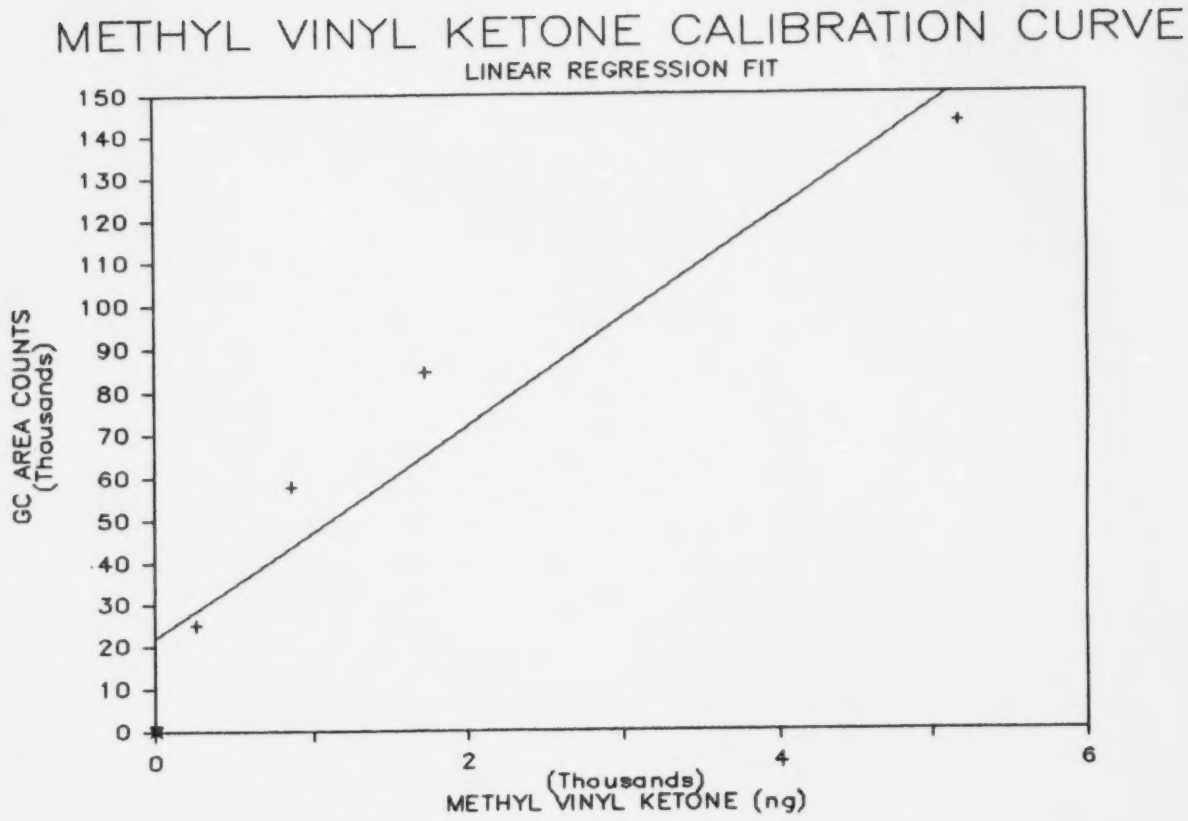


Figure 15. Calibration curve for methyl vinyl ketone.

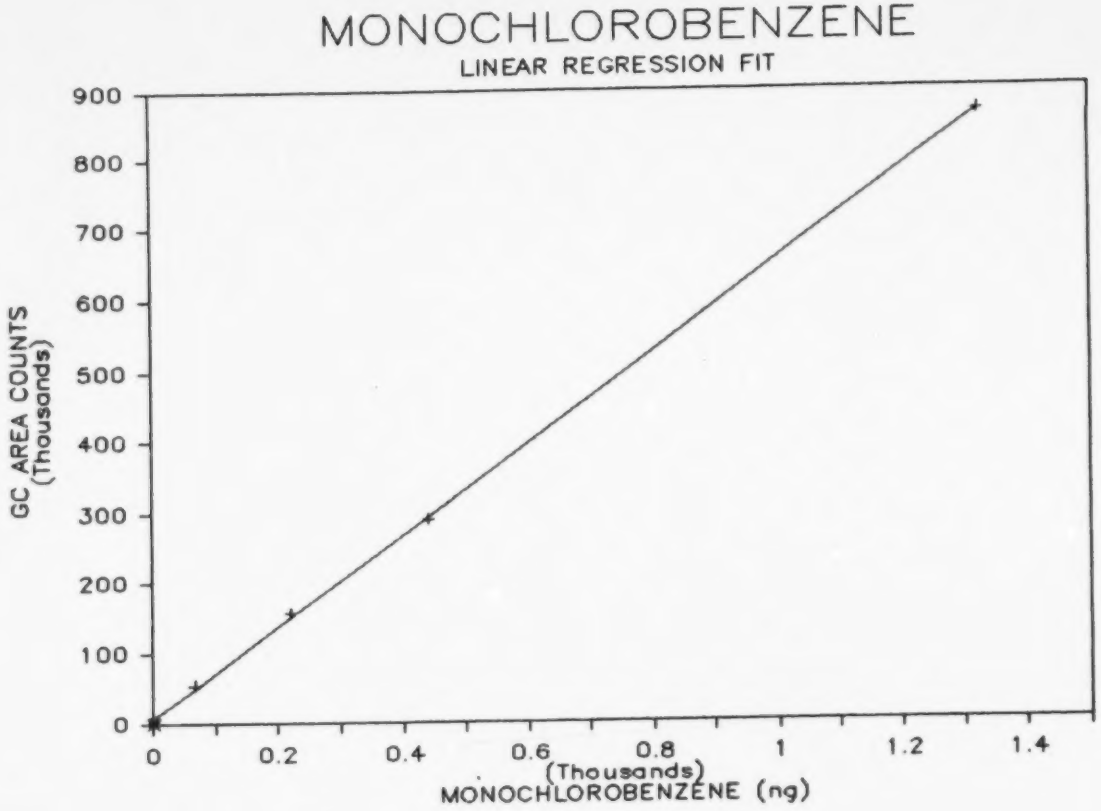


Figure 16. Calibration curve for monochlorobenzene.

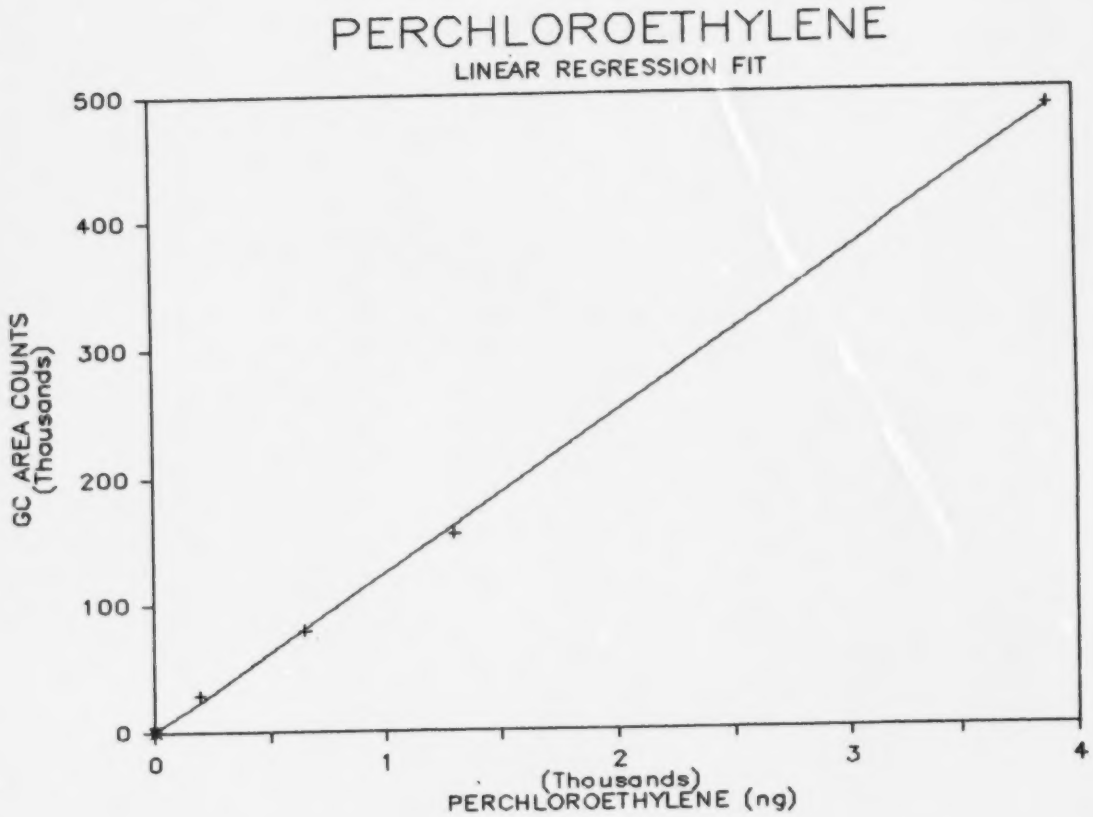


Figure 17. Calibration curve for perchloroethylene.

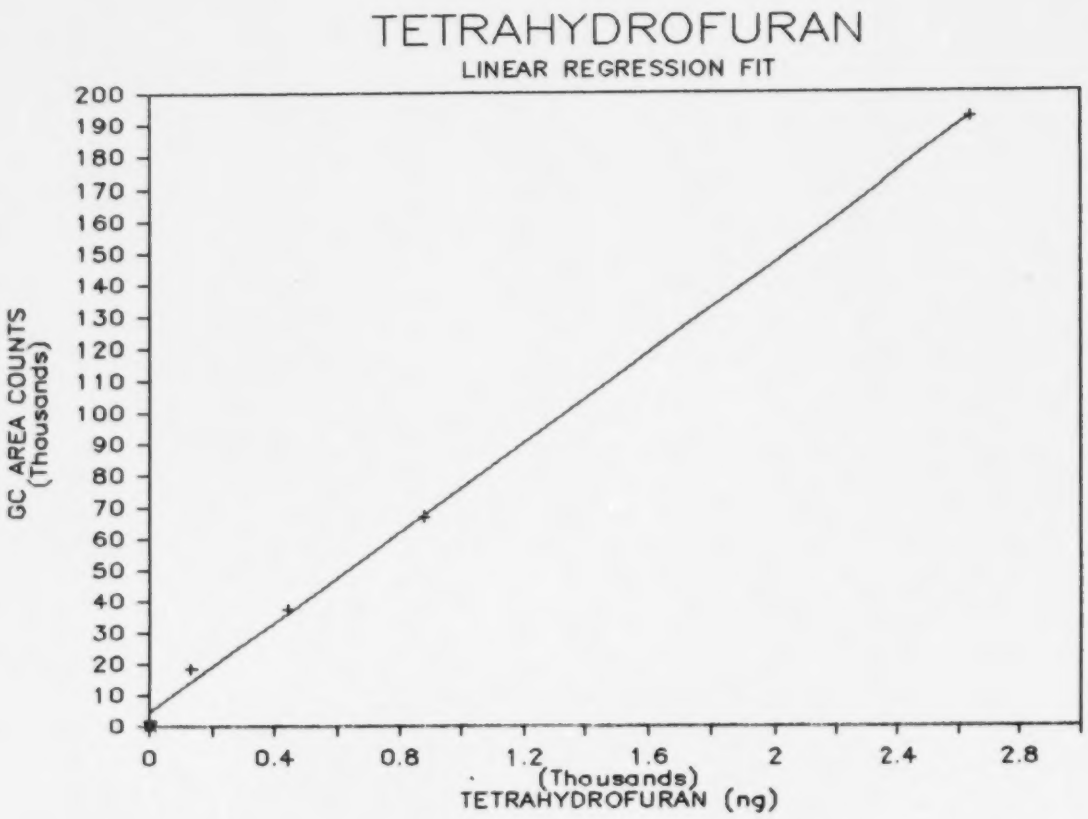


Figure 18. Calibration curve for tetrahydrofuran.

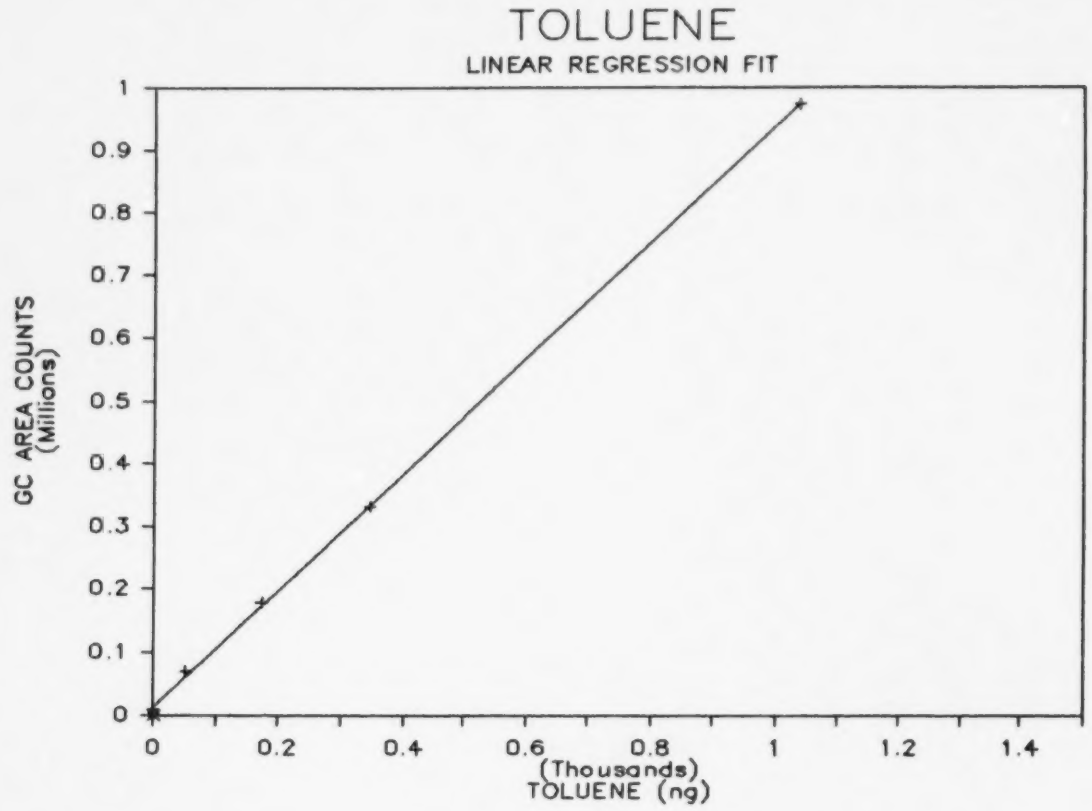


Figure 19. Calibration curve for toluene.

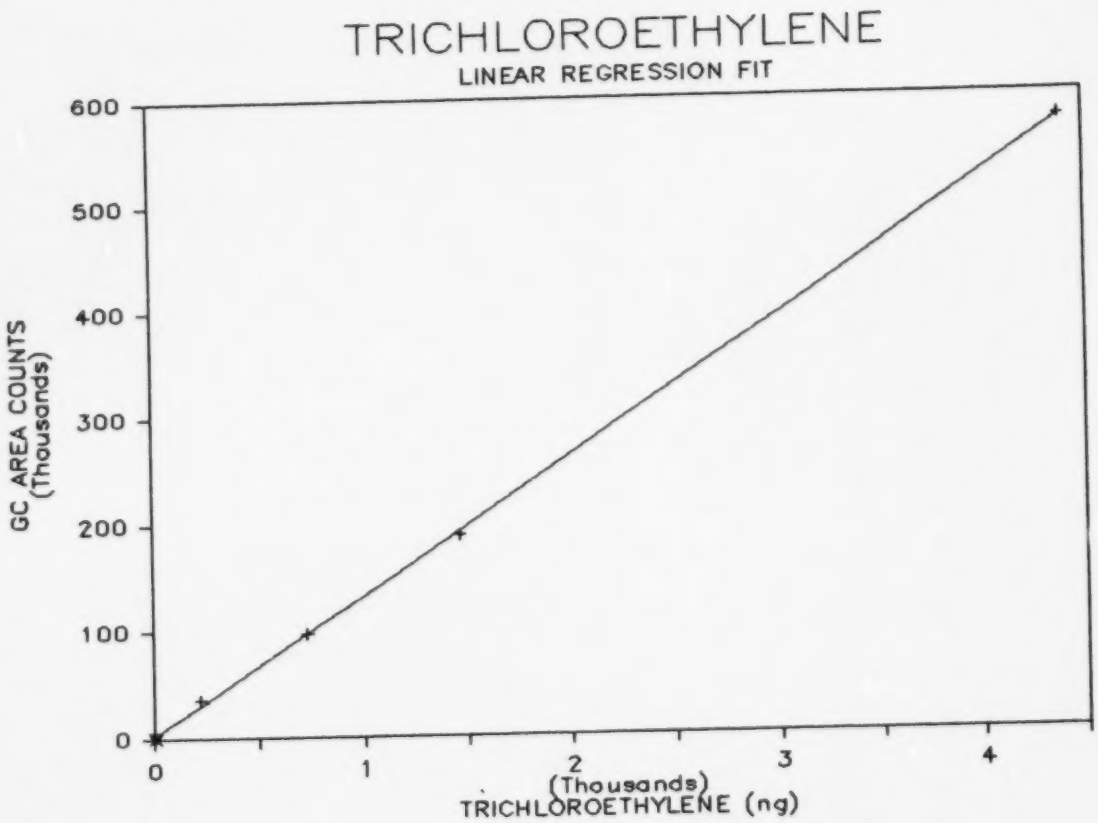


Figure 20. Calibration curve for trichloroethylene.

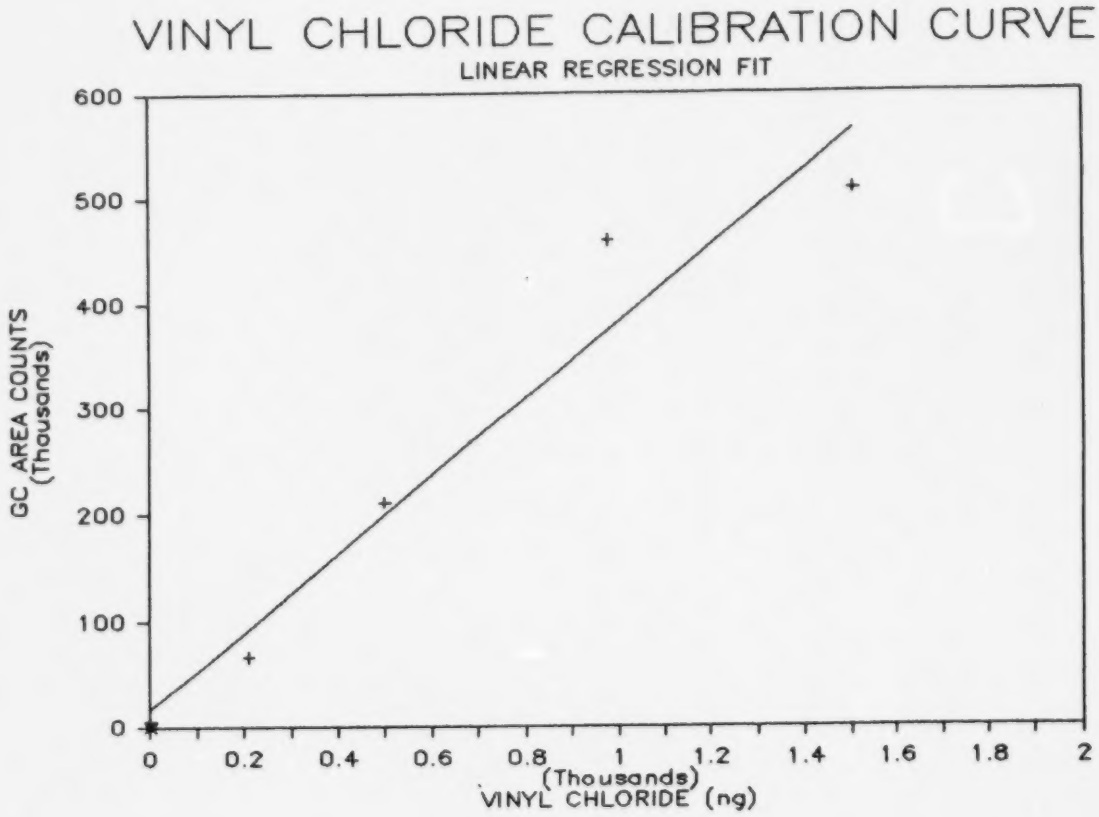


Figure 21. Calibration curve for vinyl chloride.

5.4 Sample Chromatograms and Analyses Validation

The three (3) sample traps, from each sample collection run, were analyzed in the following order: charcoal-only tube, 1.0 gram Tenax®-only tube, and 1.6 grams Tenax®-only tube. This minimized any carry over from a high concentration sample to a low concentration sample, as stated in Section 4.6. Sample chromatograms from the second sample collection run of the medium concentration level are shown in Figures 22 through 24, listed in order of analysis. Each trap was spiked with the internal standard, BFB, which was used for sample analysis validation. The criteria for acceptable analysis was a 10 percent or less deviation of the internal standard response from the daily BFB cumulative response mean. Since the BFB recovery from charcoal is low, poor BFB responses from charcoal-only traps did not invalidate those analyses.

An overall mean BFB response from GC/FID was calculated from the BFB responses from all standard, blank, and sample tube analyses, except for charcoal-only tube analyses. The compiled daily and overall means are shown in Table 7. As a further analysis validation check, the daily BFB response was then compared to the overall mean response value. As shown in Figure 25, no daily mean BFB response varied from the overall mean BFB response by more than $\pm$ 2 limits. And only one daily mean response varied from the overall mean response by more than $\pm$ 1 limits. Thus, all VOST train sample trap analyses were found to be valid.

5.5 POHC Recovery Efficiencies

After completion of GC/FID VOST train sample analyses, the expected concentrations of the POHCs in the generation system were compared to that found by the GC/FID analyses. The percent recovery of each POHC from the VOST train sampling traps was found by determination of the ratio of the GC/FID analysis result to the expected value. This was done for each compound from each sampling run analysis at each concentration level, as shown in Table 8. The average recovery percentages for each compound from each concentration level were then compiled to determine the overall average recovery percentages, which is listed in Table 9. Except for methyl vinyl ketone and vinyl chloride, the overall percent recoveries for the individual compounds ranged from 81.03% for tetrahydrofuran to 118.1% for chloroform. Vinyl chloride had an overall mean percent recovery of 55.23%, while methyl vinyl ketone had an overall mean recovery of 37.8%.

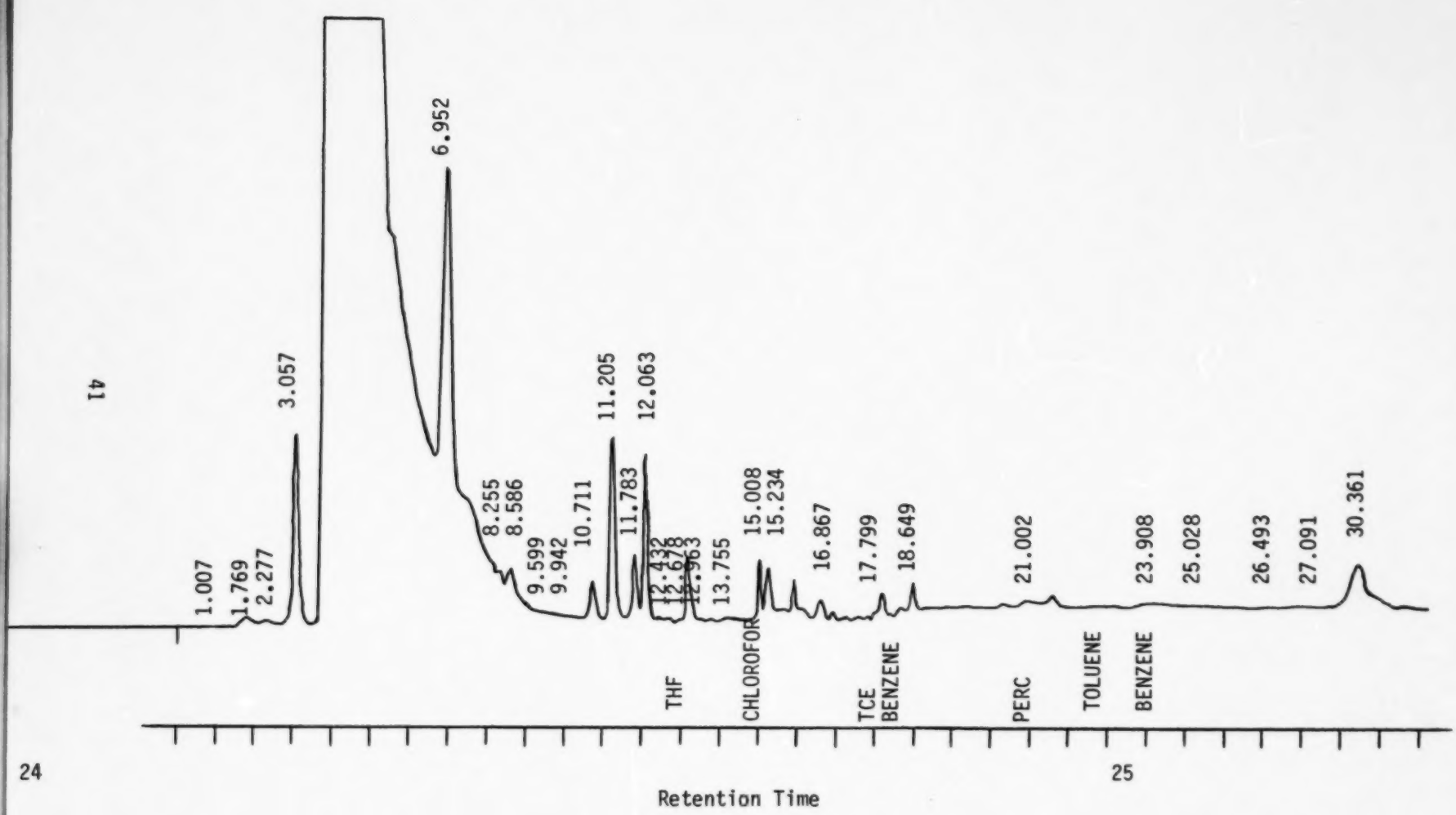


Figure 22. GC/FID chromatogram of sample trap: medium concentration level, run two, charcoal-only trap.

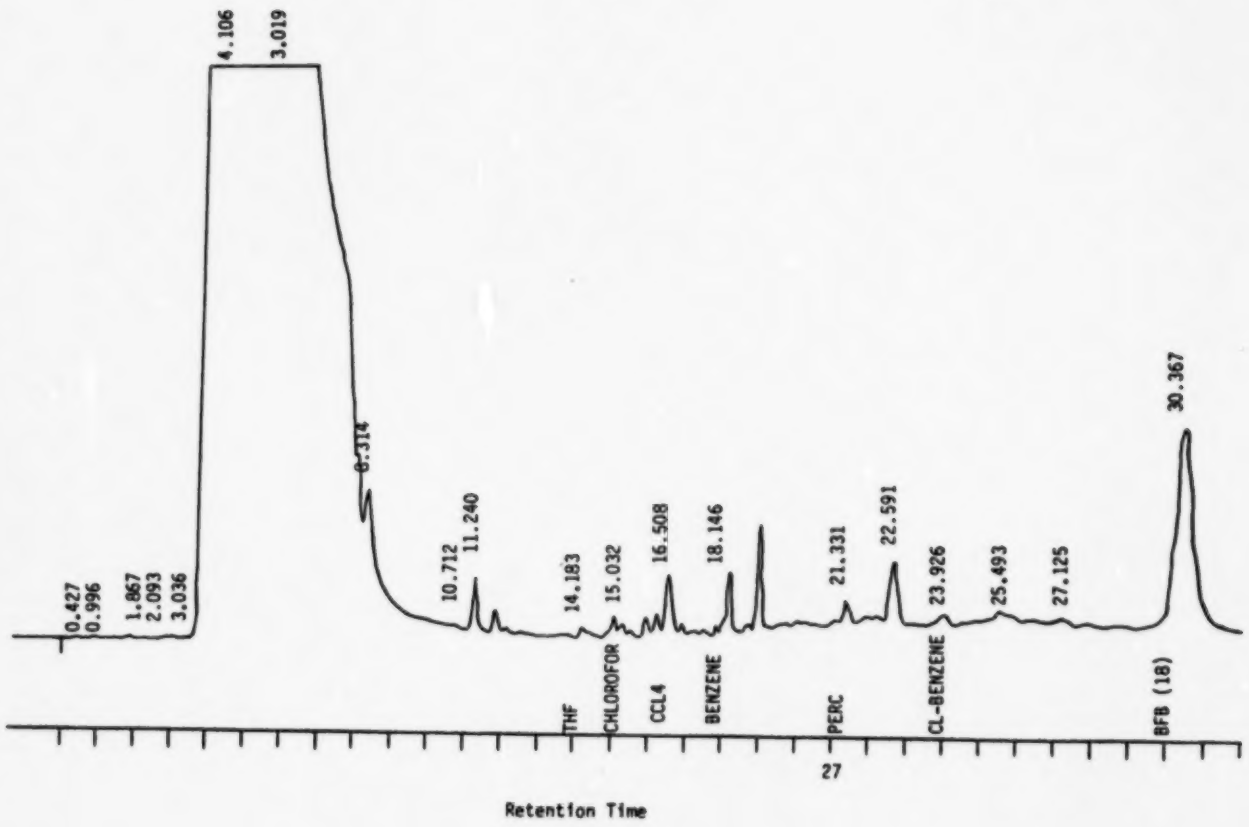


Figure 23. GC/FID chromatogram of sample trap: medium concentration level, run two, 1.0 g Tenax-only trap.

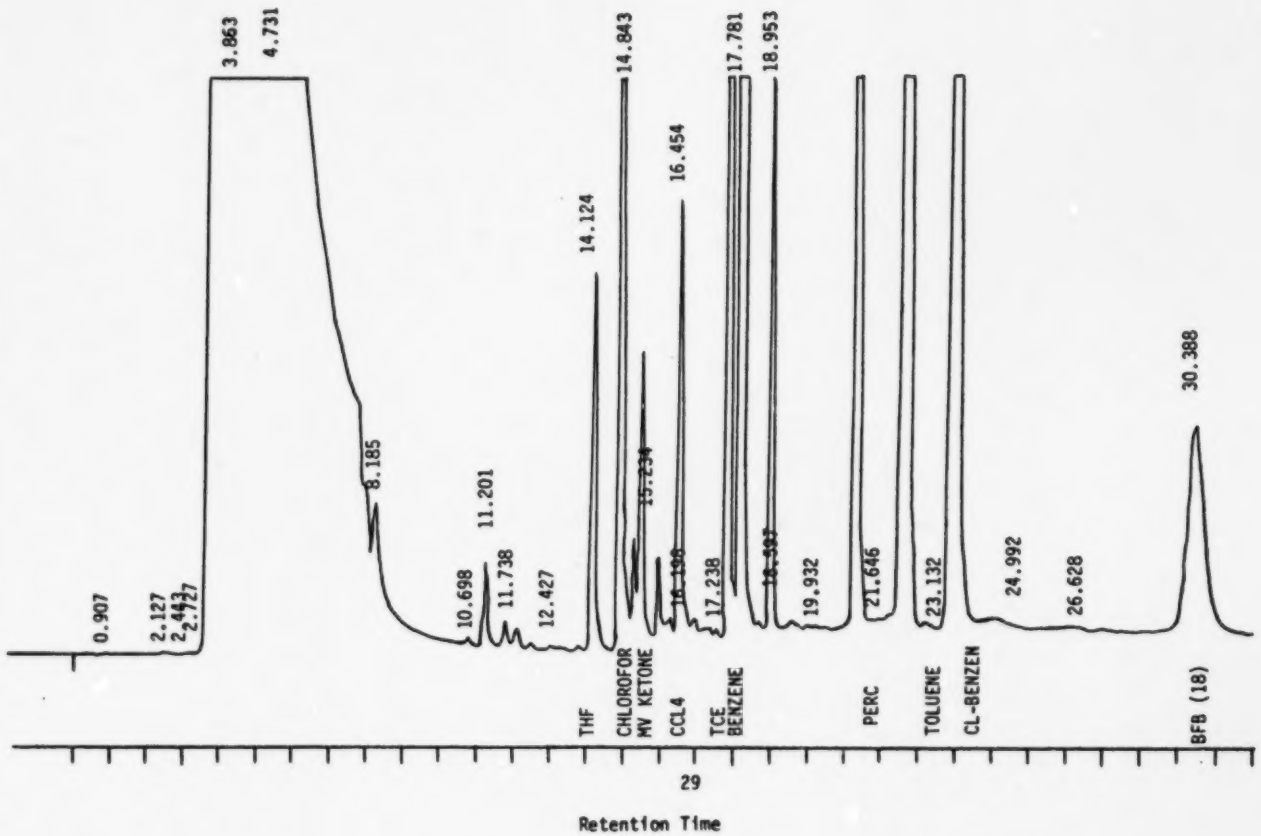


Figure 24. GC/FID chromatogram of sample trap: medium concentration level, run two, 1.6 g Tenax-only trap.

Table 7. OVERALL MEAN AND DAILY MEAN INTERNAL STANDARD* GC/FID RESPONSE VALUE

Analysis Day	Date	No. Runs	Mean BFB Value (Area Counts)	Std.Dev.( ) (Area Counts)	2 (Area Counts)	3 (Area Counts)
Overall Mean		53	153676	17753	35506	53259
1	3/23/84	1	143293	--	--	--
2	3/26/84	3	141660	4304	--	--
3	3/27/84	8	142229	14859	--	--
4	3/30/84	3	156579	3261	--	--
5	4/2/84	2	156452	8430.	--	--
6	4/3/84	1	175031	--	--	--
7	4/4/84	3	160278	16276	--	--
8	4/5/84	5	154928	15375	--	--
9	4/6/84	6	162454	18193	--	--
10	4/9/84	2	144591	3924	--	--
11	4/11/84	4	158682	11521	--	--
12	4/12/84	7	165306	28838	--	--
13	4/13/84	5	140577	12907	--	--
14	4/16/84	3	155640.	19301	--	--

*Bromofluorobenzene

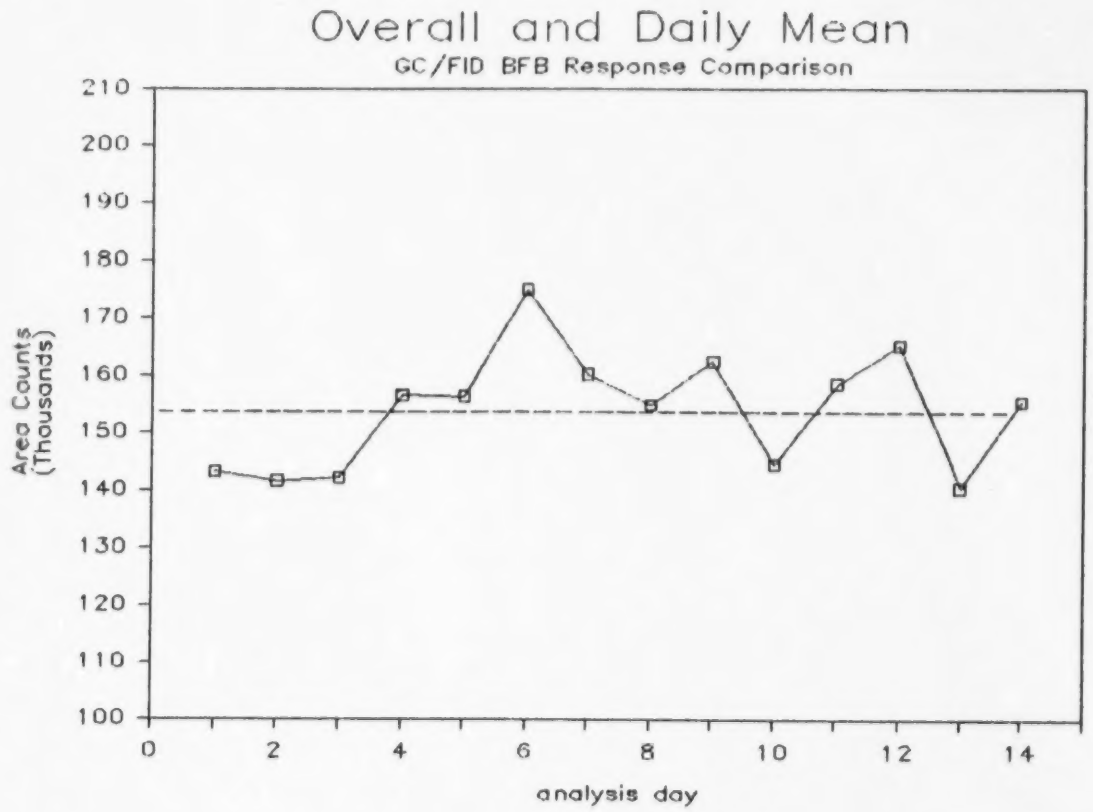


Figure 25. Overall and daily mean GC/FID BFB response comparison.

Table 8. PERCENT RECOVERIES OF POHCs FROM VOST TRAP

Compound	Low Concentration Level				Medium Concentration Level				High Concentration Level			
	Sampling Run 1 (%)	Sampling Run 2 (%)	Sampling Run 3 (%)	Average Recovery (%)	Sampling Run 1 (%)	Sampling Run 2 (%)	Sampling Run 3 (%)	Average Recovery (%)	Sampling Run 1 (%)	Sampling Run 2 (%)	Sampling Run 3 (%)	Average Recovery (%)
Benzene	97.51	104.5	88.58	96.9	123.3	104.6	92.20	106.7	67.42	75.01	87.49	76.6
Carbon Tetrachloride	124.7	90.03	39.40	84.7	73.39	149.7	151.7	124.9	128.6	132.1	171.6	144.1
Chloroform	134.7	157.1	77.16	123.0	106.5	98.43	134.3	113.1	110.2	113.7	130.7	118.2
Methyl Vinyl Ketone	0.00	28.32	0.00	9.4	50.36	29.83	44.4	41.5	40.98	65.46	80.97	62.5
Monochlorobenzene	100.7	108.1	91.05	99.9	80.81	115.2	100.3	98.8	72.95	81.80	97.20	84.0
Perchloroethylene	122.3	129.7	106.7	119.6	131.7	119.8	101.1	117.5	73.72	79.58	98.70	84.00
Tetrahydrofuran	124.0	79.55	84.54	96.0	57.76	79.73	76.71	71.4	59.64	74.03	93.27	75.7
Toluene	98.99	108.2	86.68	97.9	80.21	118.7	103.6	100.8	72.81	83.65	104.1	86.9
Trichloroethylene	100.1	106.9	84.76	97.3	76.74	112.9	97.89	95.8	72.03	80.90	94.48	82.5
Vinyl Chloride	53.13	12.65	13.23	26.3	122.8	75.60	57.01	85.1	N/A*	59.63	48.89	54.3

*Charcoal tube broke prior to analysis.

NOTE: Percent Recovery$_x$ = $\frac{\text{GC/FID analysis result}}{\text{Theoretical amount}}$ x 100%, where x = Compound X

Table 9. OVERALL MEAN PERCENT RECOVERIES OF POHCs FROM VOST TRAPS

Compound	Low Concentration Level Average Recovery (%)	Medium Concentration Level Average Recovery (%)	High Concentration Level Average Recovery (%)	Overall Average Recovery (%)
Benzene	96.9	106.7	76.6	93.40
Carbon Tetrachloride	84.7	124.9	144.1	117.9
Chloroform	123.0	113.1	118.2	118.1
Methyl Vinyl Ketone	9.4	41.5	62.5	37.8
Monochlorobenzene	99.95	98.8	83.98	94.2
Perchloroethylene	119.6	117.5	84.0	107.0
Tetrahydrofuran	96.0	71.4	75.7	81.0
Toluene	97.96	100.8	86.9	95.2
Trichloroethylene	97.3	95.8	82.5	91.9
Vinyl Chloride	26.3	85.1	54.3	55.2

Those recovery percentages greater than 100% are most likely due to a variation in the FID calibration response curve, for compounds such as chloroform and carbon tetrachloride, which were noted in Section 5.3 to have a non-linear response curve. Any positive biasing by the FID for any compound should have been accounted for by blank correction.

Erratic and poor recovery percentages for methyl vinyl ketone are not surprising. The stability of methyl vinyl ketone, as noted in Section 5.2, was of concern. The possible degradation could have not only affected the calibration curve over time but also have altered the amount of methyl vinyl ketone adsorbed onto the sampling trap.

Vinyl chloride also has poor percent recoveries, most likely since thermal desorption does not tend to drive off vinyl chloride from activated charcoal as effectively as other organics from Tenax®. Solvent extraction by CS_2 was done for the charcoal-only traps from the high concentration level. Since each trap contained 1.0 gram of charcoal, the vinyl chloride was extracted with 4.0 mL of CS_2. From the resulting solution, 2 uL were injected directly onto the GC column and analyzed by GC/FID. No vinyl chloride was detected. Since the expected amount of vinyl chloride, remaining on the charcoal trap after the thermal desorption, was extracted with 4 mL CS_2, the amount of vinyl chloride present in the portion injected onto the column was probably below the detection limit of the GC/FID.

5.6 POHC Content Per Sample Trap

As an additional check on the efficiency of the sorbent, the total POHC content found for each sample collection run was broken down to show what percentages of the total came from each of the three (3) traps used for each run. This was determined by calculating the ratio of the nanograms of compound found on a given trap to the total nanograms of compound found for that sampling run. This was determined for each sample trap of each sample collection run from each concentration level, as shown in Table 10. The average percentages of the total amount found on each trap were used to determine overall mean percentages, as shown in Table 11. The sample gas flowed through the traps during sampling in the following order: 1.6 grams Tenax®-only trap, 1.0 gram Tenax®-only trap, and 1.0 gram charcoal-only trap. Therefore, the first sample trap, 1.6 grams Tenax®-only trap, is expected to contain the highest percentage of each compound. This is true for all

compounds except vinyl chloride which is known to have poor retention on Tenax®. For each of these compounds, excluding vinyl chloride, no more than 10% of the total compound content broke through the first sample trap, with only three having greater than 5% breakthrough. Vinyl chloride had a constant breakthrough of 100% past Tenax® onto the activated charcoal.

Distribution data generated from Tenax® and Tenax®/charcoal tubes collected at the inlet and exit of a wet scrubber presented in Appendix A compares favorably with the data developed in this task. Low boiling compounds (BP <14°C) such as methyl chloride and vinyl chloride are collected on the second VOST tube containing charcoal. Chloroform, benzene, toluene, perchloroethylene, and chlorobenzene which have higher boiling points and larger retention volumes on Tenax® are predominantly collected on the first VOST tube.

Table 10. PERCENT OF TOTAL POHC CONTENT DESORBED FROM EACH SAMPLE COLLECTION TRAP

			Benzene (%)	Carbon Tetrachloride (%)	Chloroform (%)	Methyl Vinyl Ketone (%)	Monochlorobenzene (%)
Low Concentration Level	Sampling Run 1	Trap #1	100.0	89.0	99.2	0.0	100.0
		Trap #2	0.0	2.6	0.8	0.0	0.0
		Trap #3	0.0	8.4	0.0	0.0	0.0
	Sampling Run 2	Trap #1	100.0	87.4	90.4	100.0	100.0
		Trap #2	0.0	11.5	2.5	0.0	0.0
		Trap #3	0.0	1.1	6.9	0.0	0.0
	Sampling Run 3	Trap #1	100.0	84.5	67.2	0.0	100.0
		Trap #2	0.0	15.5	10.9	0.0	0.0
		Trap #3	0.0	0.0	21.9	0.0	0.0
	Average % of Total Content	Trap #1	100.0	81.0	85.7	33.3	100.0
		Trap #2	0.0	9.9	4.7	0.0	0.0
		Trap #3	0.0	9.2	9.6	0.0	0.0
Medium Concentration Level	Sampling Run 1	Trap #1	61.1	90.9	98.3	29.1	100.0
		Trap #2	0.0	0.0	1.7	70.9	0.0
		Trap #3	38.9	9.1	0.0	0.0	0.0
	Sampling Run 2	Trap #1	100.0	90.3	97.3	100.0	100.0
		Trap #2	0.0	9.7	0.8	0.0	0.0
		Trap #3	0.0	0.0	1.9	0.0	0.0
	Sampling Run 3	Trap #1	100.0	94.7	100.0	100.0	100.0
		Trap #2	0.0	5.3	0.0	0.0	0.0
		Trap #3	0.0	0.0	0.0	0.0	0.0
	Average % of Total Content	Trap #1	87.0	92.0	98..	76.4	100.0
		Trap #2	0.0	5.0	0.6	23.6	0.0
		Trap #3	13.0	3.0	0.4	0.0	0.0
High Concentration Level	Sampling* Run 1	Trap #1	100.0	100.0	100.0	100.0	100.0
		Trap #2	0.0	0.0	0.0	0.0	0.0
	Sampling Run 2	Trap #1	100.0	96.1	99.9	100.0	100.0
		Trap #2	0.0	3.9	0.0	0.0	0.0
		Trap #3	0.0	0.0	0.1	0.0	0.0
	Sampling Run 3	Trap #1	100.0	81.0	99.9	100.0	100.0
		Trap #2	0.0	19.0	0.1	0.0	0.0
		Trap #3	0.0	0.0	0.0	0.0	0.0
	Average % of Total Content	Trap #1	100.0	92.4	99.9	100.0	100.0
		Trap #2	0.0	7.6	0.1	0.0	0.0
		Trap #3	0.0	0.0	0.0	0.0	0.0

(Continued)

Table 10. PERCENT OF TOTAL POHC CONTENT DESORBED FROM EACH SAMPLE COLLECTION TRAP (Continued)

			Perchloro-ethylene (%)	Tetrahydro-furan (%)	Toluene (%)	Trichloro-ethylene (%)	Vinyl Chloride (%)
Low Concentration Level	Sampling Run 1	Trap #1	100.0	59.3	100.0	100.0	0.0
		Trap #2	0.0	0.0	0.0	0.0	0.0
		Trap #3	0.0	40.7	0.0	0.0	100.0
	Sampling Run 2	Trap #1	100.0	100.0	96.8	100.0	0.0
		Trap #2	0.0	0.0	3.2	0.0	0.0
		Trap #3	0.0	0.0	0.0	0.0	100.0
	Sampling Run 3	Trap #1	100.0	100.0	100.0	100.0	0.0
		Trap #2	0.0	0.0	0.0	0.0	0.0
		Trap #3	0.0	0.0	0.0	0.0	100.0
	Average % of Total Content	Trap #1	100.0	86.4	98.9	100.0	0.0
		Trap #2	0.0	0.0	1.1	0.0	0.0
		Trap #3	0.0	13.6	0.0	0.0	100.0
Medium Concentration Level	Sampling Run 1	Trap #1	98.5	100.0	99.8	100.0	0.0
		Trap #2	1.3	0.0	0.0	0.0	0.0
		Trap #3	0.2	0.0	0.2	0.0	100.0
	Sampling Run 2	Trap #1	98.5	100.0	98.7	100.0	0.0
		Trap #2	1.5	0.0	1.3	0.0	0.0
		Trap #3	0.0	0.0	0.0	0.0	100.0
	Sampling Run 3	Trap #1	99.3	100.0	99.8	100.0	0.0
		Trap #2	0.5	0.0	0.2	0.0	0.0
		Trap #3	0.2	0.0	0.0	0.0	100.0
	Average % of Total Content	Trap #1	98.8	100.0	99.4	100.0	0.0
		Trap #2	1.1	0.0	0.5	0.0	0.0
		Trap #3	0.1	0.0	0.1	0.0	100.0
High Concentration Level	Sampling Run 1	Trap #1	98.7	100.0	100.0	100.0	N/A*
		Trap #2	1.3	0.0	0.0	0.0	N/A*
	Sampling Run 2	Trap #1	99.6	100.0	98.9	100.0	0.0
		Trap #2	0.2	0.0	1.1	0.0	0.0
		Trap #3	0.2	0.0	0.0	0.0	100.0
	Sampling Run 3	Trap #1	98.1	100.0	98.7	100.0	0.0
		Trap #2	1.7	0.0	1.3	0.0	0.0
		Trap #3	0.2	0.0	0.0	0.0	100.0
	Average % of Total Content	Trap #1	98.8	100.0	99.2	100.0	0.0
		Trap #2	1.1	0.0	0.8	0.0	0.0
		Trap #3	0.1	0.0	0.0	0.0	100.0

*Trap #3 broke prior to analysis.

NOTE: Trap #1 is 1.4 g Tenax®-only trap; Trap #2 is 1.0 g Tenax®-only trap; and Trap #3 is 1.0 g charcoal-only trap.

Table 11. OVERALL MEAN PERCENTAGES OF THE TOTOL POHC CONTENTS DESORBED FROM EACH SAMPLE COLLECTION TRAP

	Trap No.	Benzene (%)	Carbon Tetrachloride (%)	Chloroform (%)	Methyl Vinyl Ketone (%)	Monochlorobenzene (%)	Perchloroethylene (%)	Tetrahydrofuran (%)	Toluene (%)	Trichloroethylene (%)	Vinyl Chloride (%)
Low Concentration Level Average % of Total Content	#1	100.0	87.0	85.7	33.3	100.0	100.0	86.4	98.9	100.0	0.0
	#2	0.0	9.9	4.7	0.0	0.0	0.0	0.0	1.1	0.0	0.0
	#3	0.0	3.2	9.6	0.0	0.0	0.0	13.6	0.0	0.0	100.0
Medium Concentration Level Average % of Total Content	#1	87.0	92.0	98.5	76.4	100.0	98.8	100.0	99.4	100.0	0.0
	#2	0.0	5.0	0.8	23.6	0.0	1.1	0.0	0.5	0.0	0.0
	#3	13.0	3.0	0.6	0.0	0.0	0.1	0.0	0.1	0.0	100.0
High Concentration Level Average % of Total Content	#1	100.0	92.4	99.9	100.0	100.0	98.8	100.0	99.2	100.0	0.0
	#2	0.0	7.6	0.1	0.0	0.0	1.1	0.0	0.8	0.0	0.0
	#3	0.0	0.0	0.1	0.0	0.0	0.1	0.0	0.0	0.0	100.0
Overall Average Percent of Total Content	#1	95.7	90.5	94.7	69.9	100.0	99.2	95.5	99.2	100.0	0.0
	#2	0.0	7.5	1.9	7.9	0.0	0.7	0.0	0.8	0.0	0.0
	#3	4.3	2.1	3.4	0.0	0.0	0.1	4.5	0.0	0.0	100.0

NOTE: Trap #1 is 1.6 g Tenax®-only trap; Trap #2 is 1.0 g Tenax®-only trap; and Trap #3 is 1.0 g charcoal-only trap.

6. QUALITY ASSURANCE/QUALITY CONTROL

The quality assurance project plan was submitted in November of 1983. The QA/QC checks and goals were discussed and established in that plan. The calibration curves were to be developed by linear regression. The correlation coefficient of any curve was not to be less than 0.900. Daily calibration checks were to be made. An internal standard, bromofluorobenzene, was to be spiked into each calibration, and sample analysis. The BFB responses were to be used to validate all analyses. The BFB response of a valid analysis was to within + 3 limits of the overall mean BFB response value. The completeness, accuracy, and precision goals were established as 90%, 90%, and 20%, respectively.

6.1 Calibration Curves

Four-point calibration curves were established for all compounds, as discussed in section 4.5. Except for carbon tetrachloride and chloroform, these response curves were developed by linear regression analysis, which is discussed in section 5.3. The correlation coefficients, shown in Table 6, ranged from 0.9522 for methyl vinyl ketone to 0.99988 for trichloroethylene. Since no correlation coefficient was less than 0.900, all of the response curves fitted by linear regression satisfied the established QA requirement.

6.2 Calibration Checks for Internal Standard

Daily calibration checks were made. No sample analyses were made, until the responses of these checks fell within the 95 percent confidence calibration curve.

The BFB responses from all calibration checks and sample analyses were averaged to find the overall mean BFB response value, as discussed in section 5.4 and shown in Table 7. No daily mean BFB response value varied from the overall mean BFB response by more than $\pm$ 2 limits, as shown in Figure 25. Only one daily mean BFB response varied from the overall mean response by more than $\pm$ 1 limits. Thus, all analyses were found to be valid, since no daily mean BFB response exceeded the $\pm$ 3 limits, set in the QA plan.

6.3 Completeness

The VOST was evaluated at 3 different concentration levels. A blank plus 3 sampling runs were collected at each level. Each blank and sampling run used 3 sampling traps. Thus, 36 sampling traps were used for sampling. Out of the total possible number of samples, 36, a total of 35 were analyzed: the charcoal-only trap from the first sampling run of the high concentration level was broken prior to analysis. Completeness is defined as:

$$C = \left(1 - \frac{\text{no. defective items}}{\text{total no. items}}\right) \times 100\%$$

Since one sample was lost, the completeness is 97.2% which satifies the QA goal of 90%.

6.4 Precision Estimate

The daily calibration checks, or control standards, plus the BFB standard solution were used for the precision estimate. The precision was determined by pooling the coefficients of variation for all the compounds in the sample, as shown in Table 12. The precision for the BFB solution was found to be 11.6%. For the control standard, precision was found to be 15.9%. Excluding methyl vinyl ketone, the precision for the control standard was found to be 12.7%. Both precision estimates, the BFB standard and the control standard, satisfy the QA goal for precision of 20%.

6.5 Accuracy Estimate

For the accuracy estimate, the expected amount of POHCs in each sample was compared to the amount of POHCs found by GC/FID analysis. As shown in Table 13, the three sampling runs were combined to find the average accuracy for each compound at each concentration level. These averages were then combined to find the overall average accuracy for each compound which is shown in Table 14. Excluding methyl vinyl ketone and vinyl chloride, the individual overall mean accuracies ranged from -18.9% for tetrahydrofuran to +18.1% for chloroform. Vinyl chloride

Table 12. PRECISION ESTIMATE

Sample	Compound	Number of Analyses	Mean Response Value (area counts)	Std. Dev. (area counts)	CV
Control Standard (1 uL)	Benzene	6	493220.	29718.6	0.0602542
	Carbon Tetrachloride	6	18312	4892.3	0.26716
	Chloroform	6	38985	7143.3	0.18323
	Methyl Vinyl Ketone	6	40843	13186	0.32284
	Monochlorobenzene	6	147129	8263.85	0.0561674
	Perchlorobenzene	6	72659	5729.4	0.078853
	Tetrahydrofuran	6	34634	2618.0	0.075591
	Toluene	6	170955	10109.7	0.0591365
	Trichloroethylene	6	88753	7100.1	0.079998
	Vinyl Chloride	5	166915	18186.9	0.108959
BFB Standard (1 uL)	Bromofluorobenzene	53	153676	17753	0.115522

Precision = pooled CV

$$= \left(\sqrt{\frac{\sum_{1}^{y} (n_x - 1) CV_x^2}{\sum_{1}^{y} (n_x - 1)}} \right) \times 100\%$$

where:

n_x = analysis number for compound x

CV_x = CV for anion x

y = total number of compounds in sample

Precision for control standard = 15.871%

Precision for BFB solution = 11.5522%

Table 13. PERCENT ACCURACIES OF POHCs PER CONCENTRATION LEVEL

Compound	Low Concentration Level				Medium Concentration Level				High Concentration Level			
	Sample			Average	Sample			Average	Sample			Average
	Run 1 (%)	Run 2 (%)	Run 3 (%)	Accuracy (%)	Run 1 (%)	Run 2 (%)	Run 3 (%)	Accuracy (%)	Run 1 (%)	Run 2 (%)	Run 3 (%)	Accuracy (%)
Benzene	-2.491	4.512	-11.42	-3.133	23.33	4.553	-7.798	6.695	-32.58	-24.98	-12.51	-23.36
Carbon Tetrachloride	24.72	-9.967	-60.60	-15.28	-26.61	49.74	51.71	24.95	28.57	32.07	71.59	44.08
Chloroform	34.67	57.11	-22.84	22.98	6.495	-1.570	34.31	13.08	10.18	13.68	30.68	18.18
Methyl Vinyl Ketone	-100.0	-71.68	-100.0	-90.56	-49.64	-70.17	-55.58	-58.46	-59.02	-34.54	-19.03	-37.53
Monochlorobenzene	0.7371	8.100	-8.952	-0.03830	-19.19	15.15	0.3219	-1.239	-27.05	-18.20	-2.795	-16.02
Perchloroethylene	22.35	29.70	6.708	19.59	31.75	19.80	1.126	17.56	-26.28	-20.42	-1.301	-16.00
Tetrahydrofuran	24.04	-20.45	-15.46	-3.957	-42.24	-20.27	-23.29	-28.60	-40.36	-25.97	-6.735	-24.36
Toluene	-1.012	8.169	-13.32	-2.054	-19.79	18.67	3.612	0.8307	-27.19	-16.35	4.059	-13.16
Trichloroethylene	0.08292	6.877	-15.24	-2.760	-23.26	12.87	-2.108	-4.166	-27.97	-20.10	-5.523	-17.86
Vinyl Chloride	-46.87	-87.35	-86.77	-73.66	22.79	-24.40	-42.99	-14.87	N/A*	-40.37	-51.11	-45.74

*Charcoal tube broke prior to analysis.

NOTE: Percent Accuracy = $\frac{\text{GC/FID analysis result - theoretical amount}}{\text{Theoretical amount}} \times 100\%$

Table 14. OVERALL MEAN PERCENT ACCURACIES OF POHCs

Compound	Low Concentration Level Average Accuracy (%)	Medium Concentration Level Average Accuracy (%)	High Concentration Level Average Accuracy (%)	Overall Average Accuracy (%)
Benzene	-3.133	6.695	-23.36	-6.6
Carbontetra-chloride	-15.28	24.95	44.08	17.9
Chloroform	22.98	13.08	18.18	18.18
Methyl Vinyl Ketone	-90.57	-58.46	-37.53	-62.2
Monochloro-benzene	-0.03830	-1.239	-16.02	-5.8
Perchloro-ethylene	19.59	17.56	-16.00	7.1
Tetrahydro-furan	-3.957	-28.60	-24.36	-18.9
Toluene	-2.054	0.8307	-13.16	-4.8
Trichloro-ethylene	-2.760	-4.166	-17.86	-8.3
Vinyl Chloride	-73.66	-14.87	-45.74	-44.8

had an overall mean accuracy of -44.8%, while methyl vinyl ketone had an overall mean accuracy of -62.2%. The QA goal was 90%, or ±10% of the true value. Including all compounds, five out of the ten compounds studied exceed this limit, while the remaining five, satisfy the goal.

As discussed in section 5.5, methyl vinyl ketone has poor percent accuracies due to a possible degradation problem. The poor percent accuracies for vinyl chloride likely occur since thermal desorption does not tend to drive off vinyl chloride from activated charcoal effectively.

7. REFERENCES

1. Protocol for the Collection and Analysis of Volatile POHCs Using VOST, EPA-600/8-84-007, NTIS No. PB84-170042, March 1984.

2. Purgeables - EPA Method 624, Fed. Reg., Vol. 44, No. 233, Monday, Dec. 3, 1979, 69530.

3. Quality Assurance Project Plan: Recovery of Principal Organic Hazardous Constituents and Products of Incomplete Combustion from a Volatile Organic Sampling Train, (Prepared for Industrial Environmental Research Laboratory, Office of Research and Development, U.S. Environmental Projection Agency, Research Triangle Park) EPA Contract No. 68-02-3174, November 1983.

APPENDIX A

Typical Recovery and Distribution Data Compiled Before and After a Wet Scrubber

LABELLED COMPOUND VOST TUBE PERCENT RECOVERIES

COMPOUND	PERCENT RECOVERIES	STD. DEV.	CV
D4 1.2DCE	86.5	22.3	25.7
d8 Toluene	75.2	22.5	29.9
Bromofluoro-benzene	79.0	28.9	36.6

Labelled compound recoveries from Tenax/Tenax-charcoal tubes loaded just prior to GC/MS analysis. environmental samples collected before and after wet scrubber.

COMPOUND PERCENT DISTRUBUTION ON TENAX/TENAX-CHARCOAL TUBES BEFORE AND AFTER A WET SCRUBBER

COMPOUND	BOILING POINT (°C)	TENAX (%)	TEN/CHAR (%)	NO. CASES	RANGE (ng)
chlor-ch4	-24	0	100	4	31 - 1448
BROMO-CH4	4.6	0	100	4	171 - 2990
VINYL-CHLR	-14	0	100	5	107 - 5299
CHLOR-ETHAN	12.4	100	0	5	311 - 1146
1.2-DCE	83.5	100	0	5	4 - 192
CHLOROFORM	62	100	0	5	5 - 59
1.1.1-TCE	74	90	10	5	24 - 494
BENZENE	80	99.4	0.6	8	194 - 9424
TOLUENE	110	99.5	0.5	8	53 - 9328
PERC	121	99.5	0.5	10	57 - 668
MONO-CHL/BEN	132	99.5	0.5	10	20 - 2405
ETHY/BENZ	136	99.5	0.5	9	36 - 1720
XYLENES	138 - 144	99.5	0.5	9	82 - 2849